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**Inland Waters Directorate**
**Western and Northern Region**

**Direction générale des eaux intérieures**
**Région de l'ouest et du nord**

# AUTOMATED WATER QUALITY MEASUREMENTS

# RED RIVER AT EMERSON, MANITOBA

# 1971-84

BY

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## ABSTRACT

Continuous water quality measurements of pH, dissolved oxygen, conductivity, chloride and temperature generated between 1971-84 using a robot monitor located on the Red River at Emerson, Manitoba were assessed.

The results have shown that the data recovery was virtually complete and the loss of data resulting from monitor failure was about 2%.

Generally the data were of good quality, but the pH and possibly the dissolved oxygen data were somewhat adversely affected by the water intake from a closed well on the shore.

The monitor served well in determining exceedences of parameter objectives established by the International Joint Commission. Generally, dissolved oxygen exceedences (depletion) occurred during the summer months and conductivity and chloride during the winter months, particularly during winter periods of dry years.

All parameters followed a seasonal pattern of low and high concentrations and as expected it was most evident for temperature and dissolved oxygen. Despite such a succinct seasonal pattern, the chloride, and to a lesser extent conductivity, varied substantially from year to year; reflecting the effect of varying rate of river flow and discharges from Lake Ardoch.

Prevention of sugar mill molasses discharges and the cessation of the saline water discharges from Lake Ardoch during the winter periods had a positive effect in improving the water quality.

Statistically significant long-term increases in pH, conductivity and chloride, and decrease in dissolved oxygen were observed. However, only for pH was such an increase conclusive.

## RÉSUMÉ

À l'aide d'un moniteur robotisé placé dans la rivière Rouge à Emerson (Manitoba), on a évalué la qualité de l'eau en mesurant son pH, sa conductivité, sa température et les concentrations de chlorure et d'oxygène dissous entre 1971 et 1984.

Presque toutes les données recueillies ont été récupérées, seulement 2 p. 100 d'entre elles ayant été perdues en raison du mauvais fonctionnement du moniteur.

En général, les données recueillies sont de bonne qualité. Toutefois, la présence d'un puits couvert sur la rive a quelque peu nuit à la précision des données relatives au pH et à la concentration d'oxygène dissous.

À l'aide du moniteur, on a pu déterminer si l'on avait dépassé les objectifs fixés par la Commission mixte internationale au niveau des paramètres. En général, on a observé des excédents dans la concentration d'oxygène dissous (épuisement) en été, et dans la conductivité et les concentrations de chlorure en hiver, surtout pendant les hivers des années de temps sec.

Pour tous les paramètres, on a enregistré des variations saisonnières dans les concentrations. Comme prévu, ces variations étaient plus prononcées dans le cas de la température et de la quantité d'oxygène dissous. Outre ce schéma saisonnier, les concentrations de chlorure, et à un moindre degré, la conductivité de l'eau, ont considérablement varié d'une année à l'autre, ce qui reflète l'incidence du débit changeant de la rivière et des effluents du lac Ardoch.

L'instauration de mesures préventives contre les déversements de mélasse à l'usine de fabrication de sucre et l'interruption du débit d'eau salée du lac Ardoch en hiver ont permis d'améliorer la qualité de l'eau. Sur le plan statistique, on a observé des augmentations importantes à long terme du pH, de la conductivité et des concentrations de chlorure ainsi qu'une diminution de la quantité d'oxygène dissous. Toutefois, seule l'augmentation du pH a été jugée concluante.

DISCLAIMER

Reference to trade names, commercial products, manufacturers or distributors in this report does not constitute endorsement by Environment Canada nor recommendation for use.

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# 1.0 INTRODUCTION

## 1.1 The Red River Basin

The Red River basin is part of the Hudson Bay drainage system which lies in the central portions of the North American continent. It is characterized by a broad, flat expanse of terrain, and consists mostly of lacustrine clay and till (Charron, 1969). The clay is a homogeneous deposit that contains few pebbles and varies in thickness from a few metres to more than 50 m. The till was deposited principally as ground moraine, and like the clay, it can vary in thickness from a few metres to more than 80 m. Underneath these unconsolidated surficial deposits are the shales, dolomites, limestones and sandstone that make up western plains sedimentary rocks.

The black fine textured surface soils are very fertile and produce a full range of agricultural products such as cereal, oil seeds, corn, potatoes and vegetables.

The Red River begins at the confluence of the Ottertail and Boise de Sioux Rivers near Wahpeton, North Dakota and flows northward forming the

boundary between North Dakota and Minnesota, discharging into Lake Winnipeg (Fig. 1). It is approximately 885 km. long and the drainage area above the Canada/United States boundary is 104,000 $km^2$. Most of the runoff in the watershed occurs during the spring and the least during the winter period. The 1912-1984 mean annual discharge at the boundary was 94 $m^3/s$.

Major allochthonous factors affecting the quality of the Red River are the agricultural activity in the basin, municipal and industrial waste discharges, groundwater discharge from the North Dakota sandstone formations and the discharges of saline water from Lake Ardoch. In the past, accidental municipal and industrial waste discharges resulted in oxygen depletion and fish kills in the Red River (Clarke, 1975; Gummer, 1975; Chacko, 1979). Saline water discharges from Lake Ardoch also are known to increase the chloride concentration (United States Environmental Protection Agency, 1977). In recent years these types of occurrences are not common.

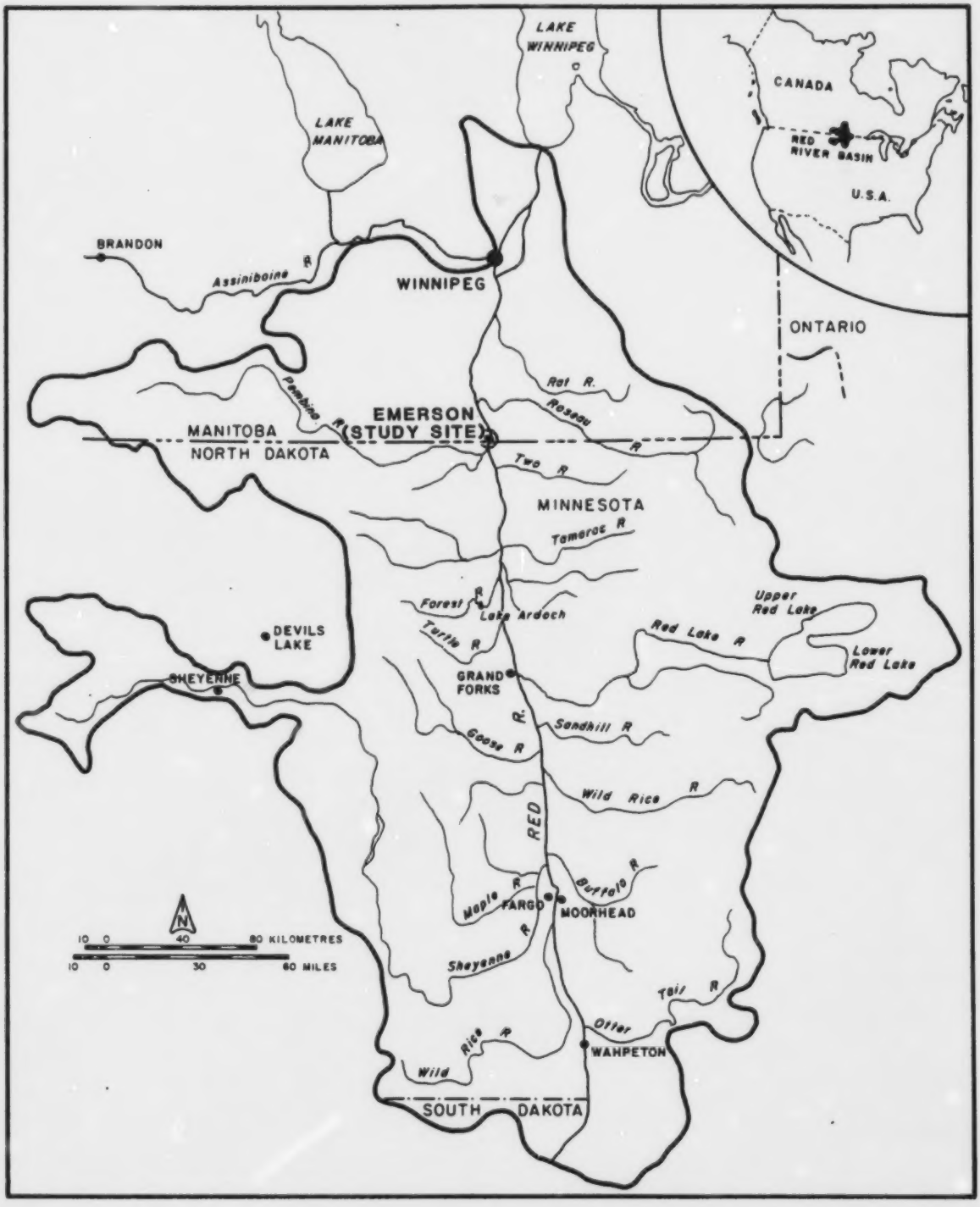


**Figure 1. Red River Basin.**

## 1.2 The Garrison Diversion Project and its Potential Adverse Effect on the Red River Water Quality

The Garrison Diversion Unit (GDU) project is a multifaceted water development scheme which, if fully implemented, would transfer water from the Missouri River to the Souris and Red Rivers and subsequently to Lake Winnipeg. Phase 1 of this project which started in 1955 does not include a transfer of water from the Missouri River to the Souris and Red Rivers. However, implementation of this project, as originally envisaged, would transfer water to these rivers and would certainly increase the levels of hardness, total dissolved solids, sulphates, sodium, total phosphorus and nitrate nitrogen (International Garrison Diversion Study Board, 1976).

The Government of Canada has maintained that water flowing from the GDU project into Canada would cause injury to health and property in Canada and would contravene Article IV of the 1909 Boundary Water Treaty. Because of stern opposition to the second phase of this project by the Governments of Canada and Manitoba as well as by environmental

conservation groups, the completion of the project has been either modified or indefinitely delayed (Garrison Diversion Unit Congressional Commission, 1984).

## 1.3 The International Joint Commission and the Red River Pollution Board

Pursuant to the provisions in Article IV of the 1909 Boundary Water Treaty, on October 1, 1964 the Governments of Canada and United States requested the International Joint Commission (IJC) to investigate the potential pollution of waters crossing the international boundary in the Red River. Following the receipt of this request, the IJC established the International Red River Pollution Board (IRRPB) on December 2, 1964. The IRRPB was provided with directives to examine the water pollution concerns and to recommend remedial measures.

The IRRPB conducted investigations in 1965-66 and submitted a report to the IJC in October, 1967. The IJC conducted public hearings and on April 11, 1968, reported to the Governments of Canada and

the United States on their findings, conclusions and recommendations. An important recommendation was that water quality objectives, as defined in the IJC report, be accepted by the Governments. The Governments of Canada and the United States accepted and approved the IJC recommendations and authorized the IJC to establish continuous supervision over the quality of water in the Red River crossing the international border. On June 10, 1969, the IJC established the current IRRPB with a new mandate.

The IRRPB carries out surveillance of the Red River water quality, informs the IJC of trends and exceedences of objectives, establishes a waste spill contingency plan and identifies future water quality issues. To carry out its mandate, the IRRPB established a continuous robot water quality monitor at the international boundary near Emerson, Manitoba which continuously measures pH, dissolved oxygen (DO), conductivity, chloride (Cl) and temperature.

## 1.4 Objectives of this Report

The objectives of this report are:

1. to assess the reliability of the data collected by the continuous water quality monitor;

2. to evaluate the extent of compliance with the IJC water quality objectives;

3. and to examine the usefulness of the monitor data in determining the water quality trends in the Red River.

## 2.0 METHODS AND PRINCIPLES OF DATA ACQUISITION

### 2.1 Schneider Model RM25A Robot Monitor*

The Schneider Model RM25A robot monitor is an automatic water quality data acquisition system incorporating a pump flow-through system, sensors and analyzers. It is composed of either three or four separate components, each housed in a water-proof, corrosion-resistant aluminum cubicle (Fig. 2). The bottom cubicle contains the sample plumbing and sensing elements while the second cubicle houses the electronic analyzer portion of the system. The data collected are either recorded on chart paper or transmitted to a computer by the output phase of the monitor. Chart measurements are recorded every six minutes and telemetry every 12 minutes.

### 2.2 Location, Maintenance and Calibration

The monitor was acquired in 1969 and was operated by the Province of Manitoba until 1971. From 1971

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* Mention of product name does not imply endorsement or recommendation for use.

on, it was operated by the Water Quality Branch (WQB), Environment Canada. It is located in the Town of Emerson water treatment plant (Fig. 3).

Water to the monitor is supplied with a 60 L/min submersible pump located in a gravity-fed well on the River shore. The water intake to the well is approximately 60 m off the shore located at midstream. The water level in the well varies with the river stage. The water turn-over in the well has been estimated to be between 2.5/hrs during the low flow condition and 0.3/hrs during high flow.

The monitor was maintained by local contracted personnel and by WQB staff. Weekly cleaning and daily visual checking for abnormalities were carried out by the contracted personnel until 1981. From 1981 on, the daily checking was done by WQB staff by viewing data transmitted via satellite telemetry. Routine monthly, or biweekly calibration and adjustments were carried out by the WQB technical staff. The calibration was accomplished by taking manual measurements and then making adjustments on the monitor

accordingly. Generally, very few adjustments were required for pH, conductivity and temperature. But, for dissolved oxygen and chloride, adjustments were required more frequently.

Drift in probe response was usually caused by sedimentation and algal growth on the sensors. When adjustments were required for probe drift prior to the time of calibration, the drift was considered to be linear and the data were adjusted from the previous calibration.

## 2.3 Principles of Data Acquisition

### 2.3.1 pH

The pH of a solution is the logarithm of the reciprocal of the hydrogen ion concentration (or hydrogen ion activity). It is measured electrically as a potential which essentially indicates whether the solution is acidic or alkaline. The pH parametric system employs a sensor assembly comprised of a pH glass electrode, a silver:silver-chloride reference electrode, a monel grounding rod and a temperature compensator. The output (volts) is proportional to the difference between the glass electrode potential and the reference electrode potential. The difference is minimum at pH 7.

### 2.3.2 Dissolved Oxygen (DO)

A polarographic electrode is used as the DO sensor. The electrode consists of a gold cathode and a group of silver anodes immersed in an internal electrolyte which is separated from the solution being analyzed by a membrane permeable to

oxygen. The cathode is connected to the negative side and the anodes are connected to the positive side of a voltage divider across a regulated reference supply. Potential across the electrode is adjusted to 0.80 direct current Volts (VDC).

Compensation is provided for the effect of temperature upon the relationship between dissolved oxygen concentrations and oxygen partial pressure, and also for the effect of temperatures on the permeability of the membrane. A solid state operational amplifier is used in a microammeter circuit to measure the electrode current.

### 2.3.3 Conductivity

Conductivity of a solution is measured by the quantity of electricity transferred across a unit area through a unit length by a unit potential gradient per unit time. It is the reciprocal of specific resistance and is generally reported as uS/cm. The conductivity cell is used as the variable input resistance of an operational amplifier with a constant input voltage. The

characteristic of the operational amplification is such that the output voltage will be inversely proportional to the input resistance. Therefore, the amplification output voltage is directly proportional to the conductivity of the solution measured. Temperature compensation is introduced by letting the temperature sensitive resistance of the compensator vary the "constant" input voltage to the amplifier.

### 2.3.4 Chlorides

The chloride parametric system employs a sensor assembly comprised of a chloride ion billet electrode, a silver:silver-chloride reference electrode and a temperature compensator. The use of the silver:silver-chloride reference electrode for measurement of the concentrations of chloride ion in a solution is an application of oxidation-reduction potential measurement. The chloride electrode and reference electrode act as half cells. The output is in voltage proportional to the difference between the half cells.

### 2.3.5 Temperature

A silicon resistance element is used as the temperature sensor. This sensing device has a positive temperature coefficient of resistance, yielding an almost linear resistance vs temperature. It is used in a bridge circuit supplied from a regulated 5-volt DC power supply. The bridge is balanced at a sensor resistance equivalent to $-17^{o}C$, and at other temperatures the signal produced by the imbalance of the bridge circuit is measured as an indication of temperature. A solid state operational amplifier is used to measure the imbalance, to automatically linearize the characteristic, and to produce the standard analyzer outputs of 0-50 MV DC for recording and 0-1000 MV DC for telemetry.

## 2.4 Monthly (Routine) Grab Samples

Routine grab samples were collected to allow comparisons with the monitor data and to provide broad parametric coverage. Only parameters that are directly related to the monitor data are discussed in this report. The sampling procedures

and analytical methods are described in Sampling for Water Quality (Environment Canada, 1983) and Analytical Method Manual (Environment Canada, 1979).

## 2.5 Discharge Data

All discharge data used in this report are determined by the Water Resources Branch as a part of their routine monitoring network (Environment Canada, 1985).

**Figure 2** Schneider Model RM25 Robot Monitor

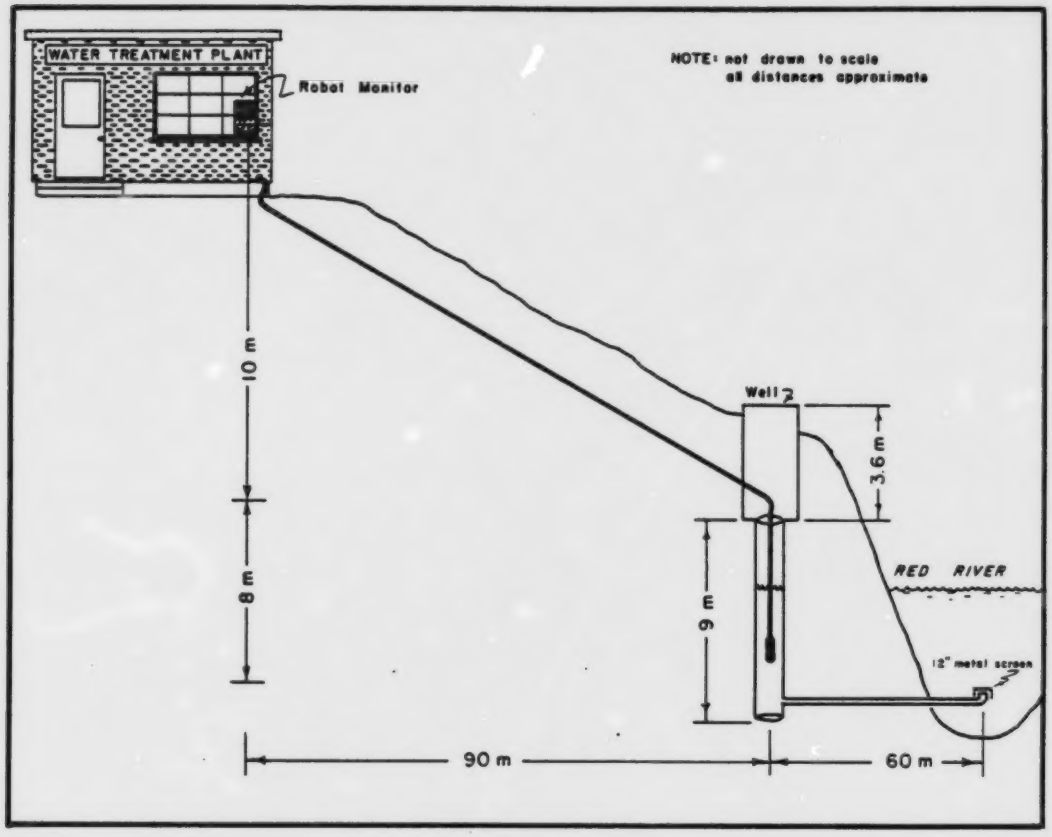



**Figure 3. Schematic Diagram of Water Intake.**

## 3.0 RESULTS

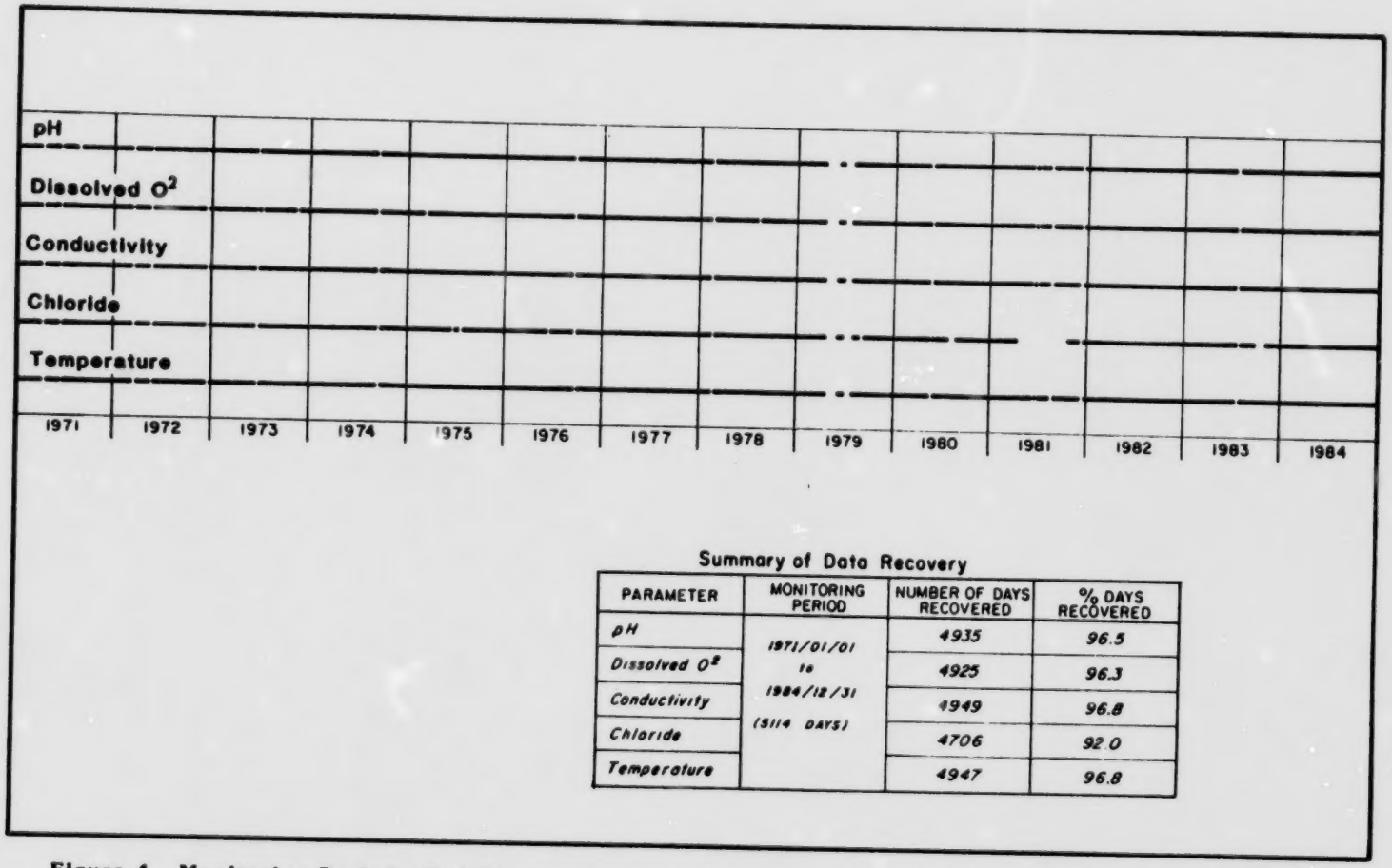
A summary of the 1971-84 monitoring record is given in Figure 4. This record indicates that for pH, DO, conductivity and temperature, the data recovery was better than 96%. For chloride, the recovery was lower, which was mostly caused by an electronic malfunction experienced in 1981. The causes of the data loss, presented in Table 1, reveal that, except for the electronic malfunction encountered with the chloride analyzer in 1981, the most common causes were the high water levels, pump failure, recorder failure and probe failure. The chloride and DO probes had more failures than others and, as expected, the temperature and conductivity probes were virtually trouble-free. Total data loss resulting from the monitor related failure was about 2%.

Summary statistics of the 1971-84 monitor daily values are presented in Table 2-a. The mean and median values suggest that except for pH, the values are skewed to the right, yielding mean values which are higher than median values. This difference is most significant for chloride and conductivity.

Summary statistics of the grab samples and monitor values of the corresponding days are also given in Tables 2-b and 2-c, respectively. Since the grab sample values are instantaneous values and the monitor values are daily means (of 240 values) a rigorous comparison is not possible. However, the mean and median values suggest that somewhat higher chloride and temperature values and lower DO values are obtained with the monitor. The reasons for these differences are dealt with in Sec. 4. Results of the paired 't' tests of the monitor and routine grab samples are presented in Table 3. Medians and number of pairs are different than in Tables 2-b and 2-c since the analysis includes only days for which values for both monitor and grab are available. These results indicate that except for conductivity, the monitor and the routine grab sample median values are different at a 95% confidence level. However, the relatively small 't' values and the high linear regression coefficients for the monitor and routine grab samples indicate that except for pH and possibly for DO, the agreement is good.

Monthly values of the above parameters averaged

for the entire study period, 1971-84, are presented in Figure 5. Variability in the mean monthly values of pH, DO, conductivity, chloride, temperature and discharge is presented in Figures 6-a,-b,-c,-d,-e,-f. Monthly means were computed from daily means which were based on 240 sequentially measured values.




Summary of Data Recovery

| PARAMETER | MONITORING PERIOD | NUMBER OF DAYS RECOVERED | % DAYS RECOVERED |
|---|---|---|---|
| pH | 1971/01/01 to 1984/12/31 (5114 DAYS) | 4935 | 96.5 |
| Dissolved $O^2$ | | 4925 | 96.3 |
| Conductivity | | 4949 | 96.8 |
| Chloride | | 4706 | 92.0 |
| Temperature | | 4947 | 96.8 |

**Figure 4. Monitoring Period - Red River at Emerson (gaps shown for missing data greater than two days).**

TABLE 1. Summary of the Causes of the Monitor Data Loss in Days*

| Cause | pH | DO | Cond | Cl | T |
|---|---|---|---|---|---|
| Removal of monitor due to high water levels: | 53 | 53 | 53 | 53 | 53 |
| Pump failure: | 38 | 38 | 38 | 38 | 38 |
| Recorder failure: | 38 | 38 | 38 | 38 | 38 |
| Probe failure: | 30 | 40 | 12 | 58 | 12 |
| Electronic problems: | 3 | 3 | 3 | 157 | 3 |
| Town of Emerson repair and cleaning of well: | 15 | 15 | 15 | 15 | 15 |
| Incorrect calibration: | 0 | 0 | 0 | 31 | 0 |

* Total days of operation 5114

TABLE 2-a. Summary Statistics - Daily Monitor Values
Red River at Emerson 1971-1984

| Parameter | Mean | Median | Std.Dev. | Min. | Max. | Range | Skewness | Number |
|---|---|---|---|---|---|---|---|---|
| pH-units | 7.89 | 7.90 | 0.37 | 6.20 | 9.50 | 3.30 | 0.18 | 4935 |
| DO mg/L | 9.49 | 9.40 | 2.25 | 0.20 | 19.00 | 18.80 | 0.21 | 4925 |
| Cond.uS/cm | 663.07 | 625.00 | 196.45 | 320.00 | 2000.00 | 1680.00 | 1.83 | 4949 |
| Cl mg/L | 48.82 | 36.00 | 42.99 | 4.00 | 437.00 | 433.00 | 2.76 | 4706 |
| T $^{o}$C | 9.76 | 8.00 | 8.96 | 0 | 30.00 | 30.00 | 0.39 | 4949 |

TABLE 2-b. Summary Statistics - Grab Samples

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| pH units | 7.98 | 8.00 | 0.33 | 7.20 | 8.90 | 1.70 | 0.02 | 162 |
| DO mg/L | 10.04 | 10.00 | 2.58 | 2.30 | 18.40 | 16.10 | 0.20 | 126 |
| Cond.uS/cm | 678.52 | 650.00 | 234.03 | 300.00 | 1580.00 | 1280.00 | 1.79 | 157 |
| Cl mg/L | 47.11 | 30.00 | 47.81 | 7.30 | 310.00 | 302.70 | 2.83 | 162 |
| T $^{o}$C | 9.15 | 6.50 | 9.13 | 0 | 26.00 | 26.00 | 0.45 | 129 |

TABLE 2-c. Summary Statistics - Monitor Values of
Corresponding Grab Sampling Days

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| pH units | 7.92 | 7.90 | 0.34 | 7.20 | 9.00 | 1.80 | 0.08 | 159 |
| DO mg/L | 9.49 | 9.60 | 2.24 | 2.50 | 16.40 | 13.90 | 0.11 | 158 |
| Cond.uS/cm | 659.40 | 635.00 | 192.42 | 330.00 | 1200.00 | 870.00 | 1.17 | 159 |
| Cl mg/L | 49.63 | 35.20 | 45.67 | 5.00 | 240.00 | 235.00 | 2.35 | 151 |
| T $^{o}$C | 9.69 | 7.90 | 8.97 | 0.10 | 29.00 | 28.90 | 0.43 | 159 |

TABLE 3. Summary Statistics - Paired 't' Values at 0.05 Sig. Level

| Parameter | Monitor Median | Grab Median | Paired No. | 't' Value | Median significantly different or not |
|---|---|---|---|---|---|
| pH Unit | 7.9 | 8 | 119 | 2.235 | yes |
| DO mg/L | 9.4 | 10 | 118 | 5.037 | yes |
| Cond.uS/cm | 641.0 | 650 | 136 | 1.295 | no |
| Cl mg/L | 35.0 | 29.5 | 146 | 4.312 | yes |
| T $^{o}C$ | 7.9 | 5 | 119 | 6.049 | yes |

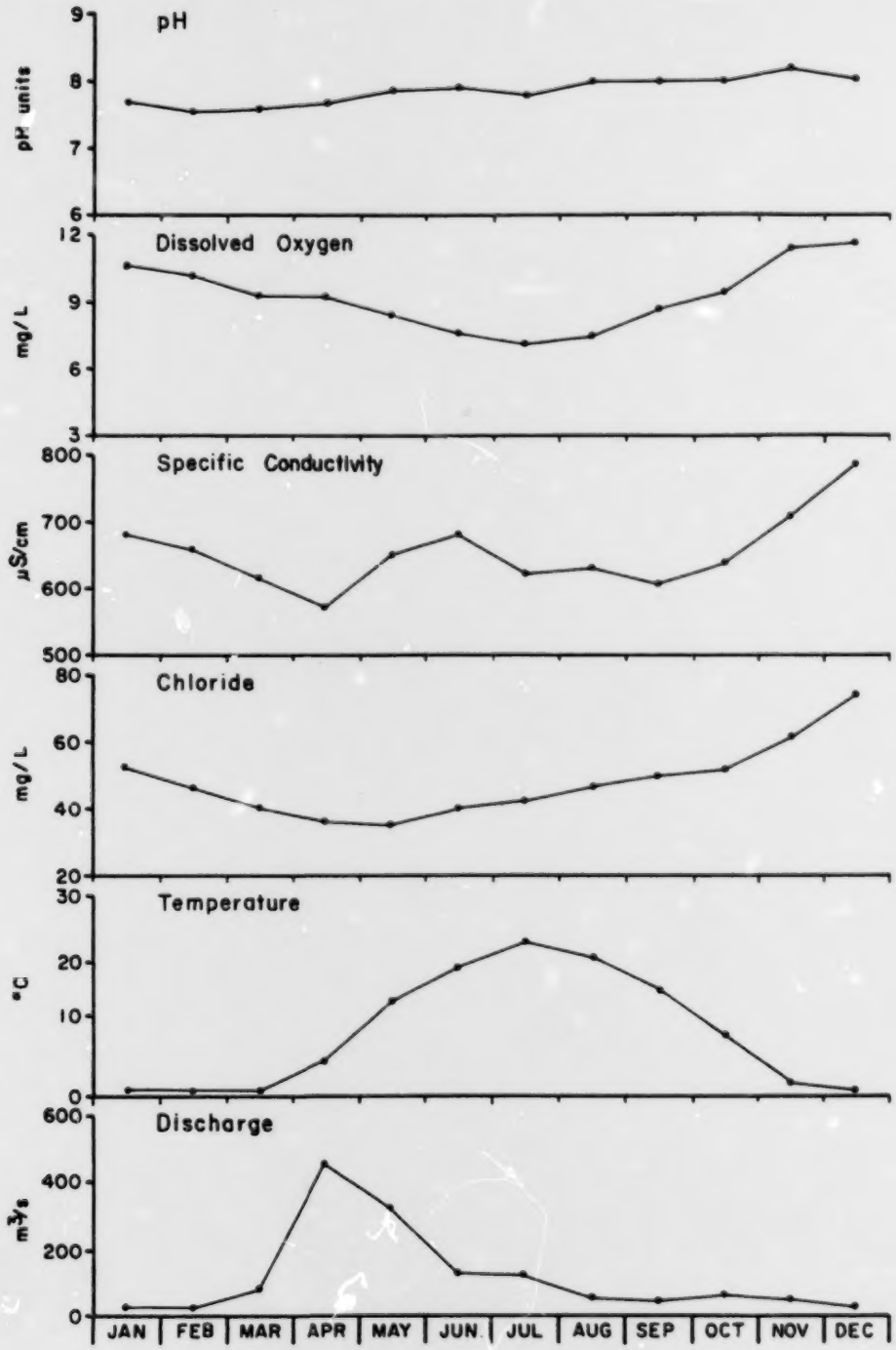



**Figure 5** Mean Monthly Concentrations - Red River at Emerson, 1971-84

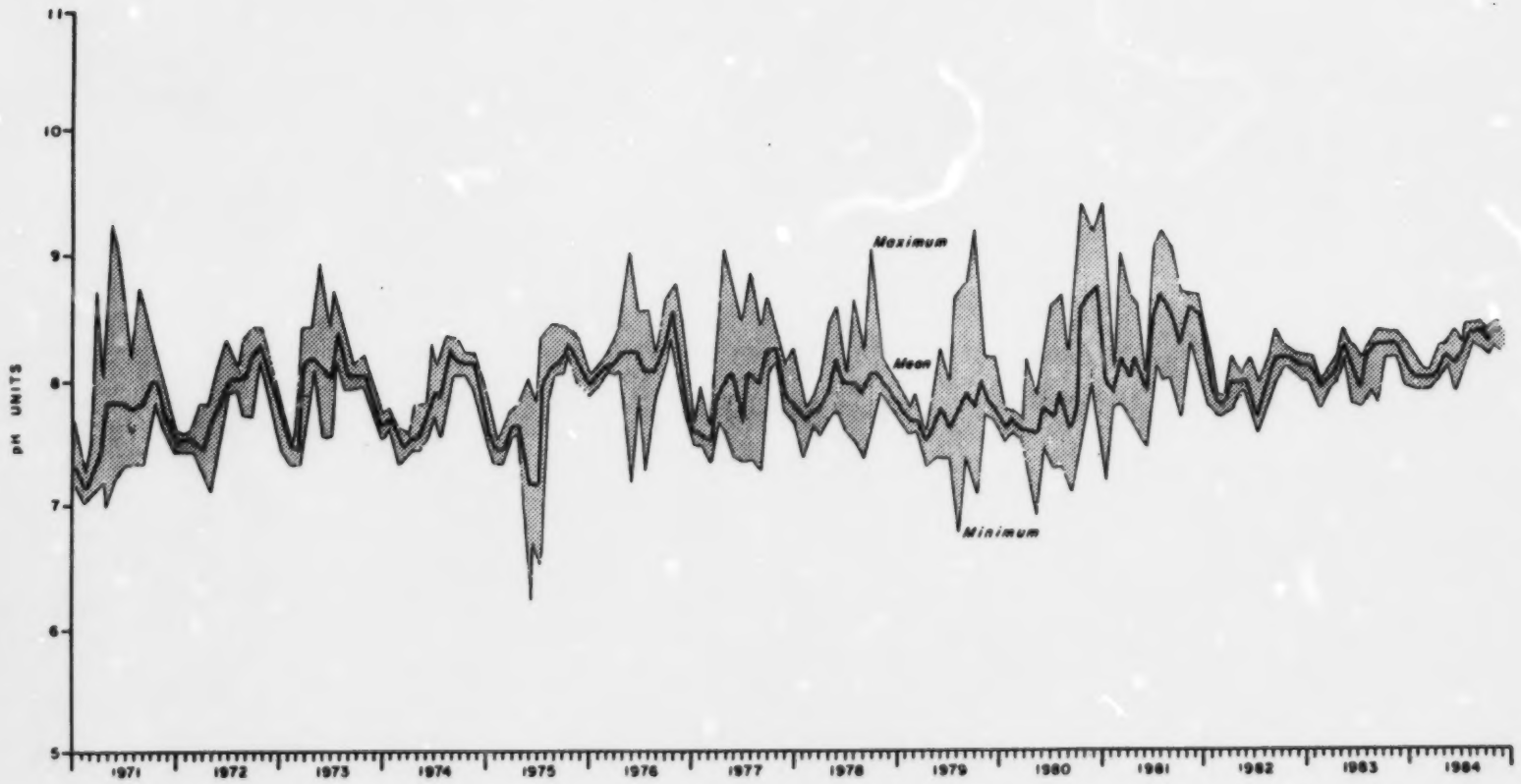



**Figure 6a** Variability in Mean Monthly pH Concentration - Red River at Emerson; Minimum and Maximum Daily Mean Concentrations are also shown.

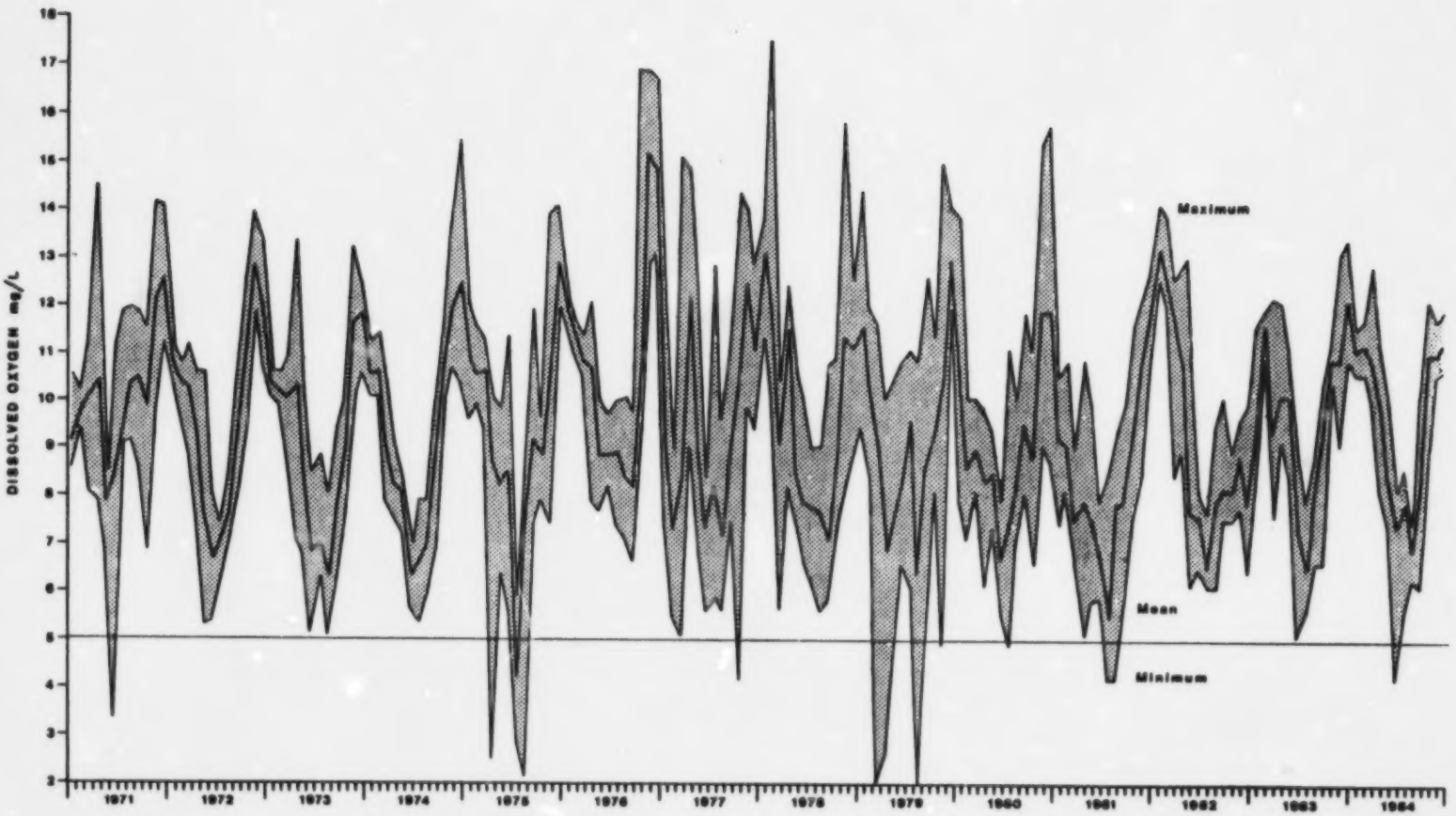



**Figure 6b** Variability in Mean Monthly DO Concentrations - Red River at Emerson; Minimum and Maximum Daily Mean Concentrations are also shown.

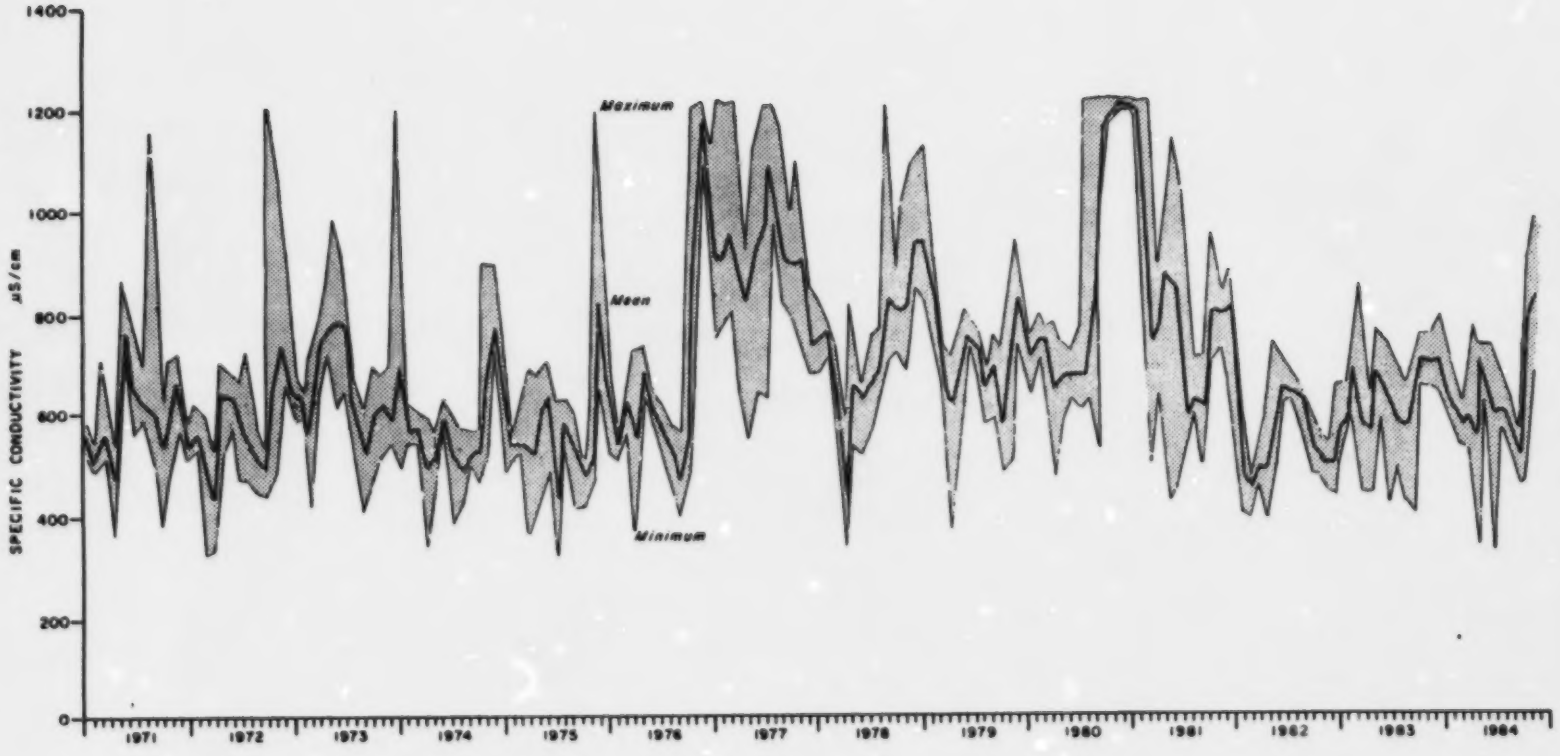



**Figure 6c** Variability in Mean Monthly Conductivity Concentration - Red River at Emerson; Minimum and Maximum Daily Mean Concentrations are also shown.

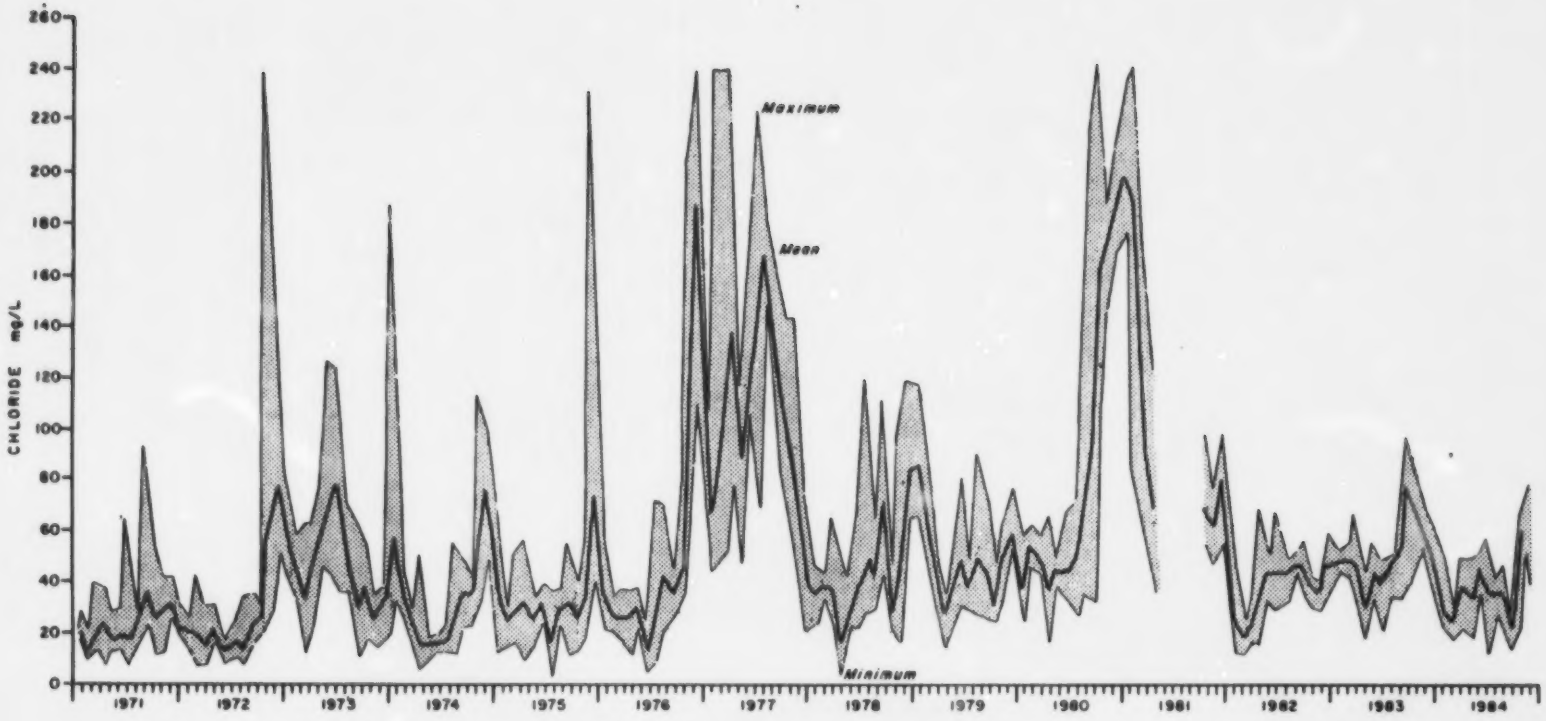



**Figure 6d** Variability in Mean Monthly Chloride Concentration - Red River at Emerson; Minimum and Maximum Daily Mean Concentrations are also shown.

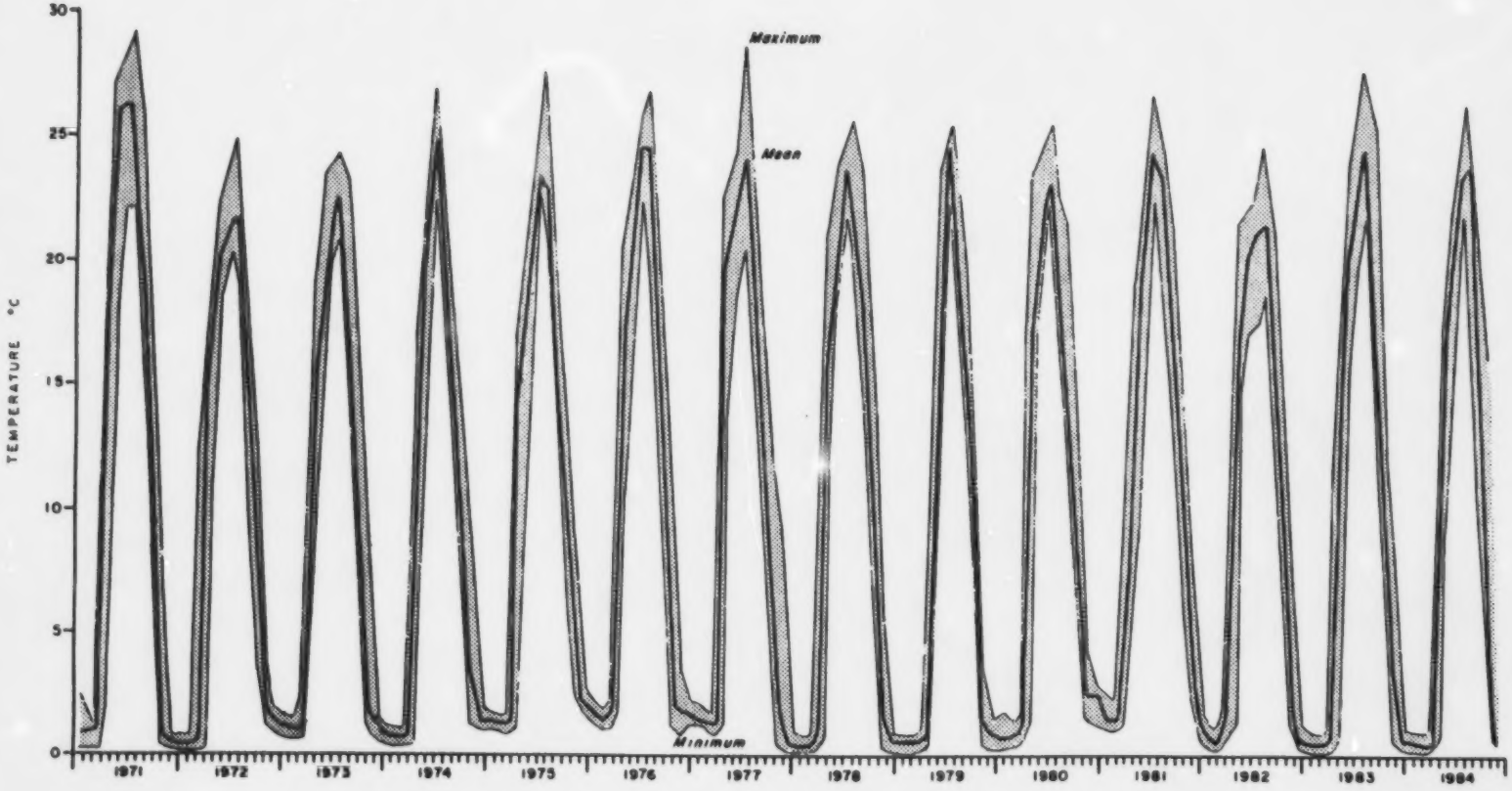



**Figure 6e** Variability in Mean Monthly Temperature - Red River at Emerson; Minimum and Maximum Daily Mean Values are also shown.

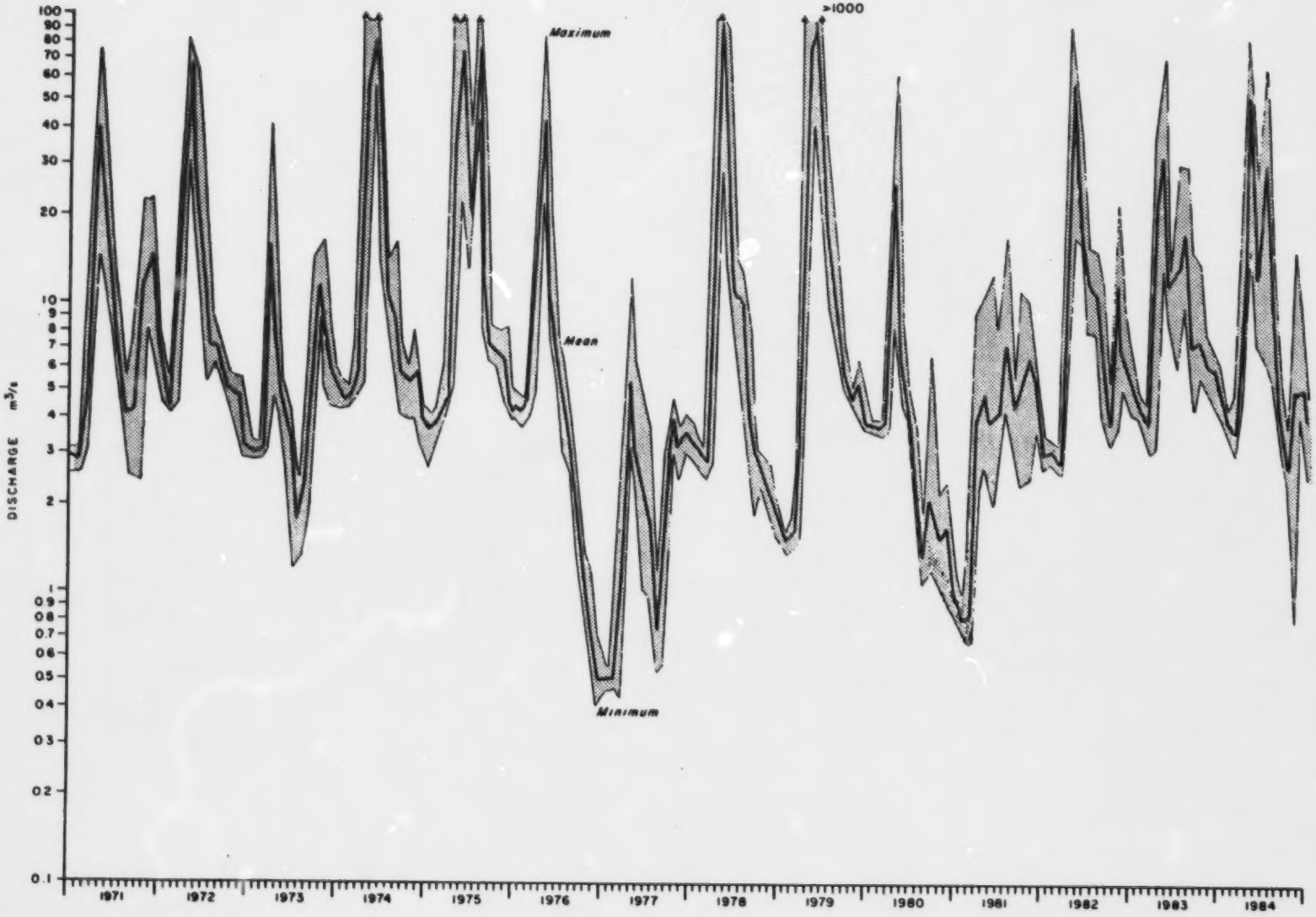



**Figure 6f** Variability in Mean Monthly Discharge - Red River at Emerson; Minimum and Maximum Daily Mean Discharges are also shown.

# 4.0 DISCUSSION

## 4.1 Reliability of the Monitor Data

Reliability of the monitor data is assessed in terms of the routine calibration, intra-relation of the monitor measured variables and in relation to the routine grab samples.

### 4.1.a Routine Calibration

As stated in Sec. 2.2, calibrations were carried out either monthly, biweekly or more frequently when deemed necessary, and the monitor values were adjusted accordingly. Analytical methods used at time of monitor calibration and routine grab sampling were identical and therefore any variation resulting from the analytical methods is considered to be minimal. When there was a need to adjust the data for probe drift during days preceding the time of calibration, the drift was considered to be linear and the data were adjusted accordingly.

Because of the daily checking, weekly cleaning and

the routine calibration protocols established and maintained for the most part, the data are considered to be of adequate quality for detecting long-term changes.

4.1.b Intra-relations of the Monitor Data

The statistical summary presented in Table 2-a reveals that the data distributions of most variables are skewed to the right, yielding higher means than median values. This was most evident for chloride and conductivity. In order to include these naturally occurring high values (not considered as spurious outliers), the mean of the data base rather than a median was used for further assessment.

Chloride and conductivity were expected to be directly related and DO and temperature to be inversely related. Regression plots of the monitor data presented in Figures 7 and 8 reveal that indeed this was the case, but the correlation (linear and nonlinear) between DO and temperature was poor. Possible explanations for this poor correlation, as discussed in Sec. 4.2, are the

effect of biological activity and the oxidation of organic substances and wastes in the Red River.

Regression plots of the routine grab chloride vs conductivity and of the monitor chloride vs conductivity for corresponding days (Figures 9 and 10) show that the correlation for the routine grab samples was somewhat better than that of the monitor. The poorer correlation of the latter, at least in part, is attributed to the poor sensitivity of the monitor chloride probe at low concentrations. Data presented in Sec. 4.1.c show that at low concentrations the monitor chloride values are somewhat higher. Regression plots of the routine grab DO vs temperature and of the monitor DO vs temperature for corresponding days (Figures 11, 12), yield similar correlations. Therefore, despite the above recognized limitations, the agreement within the monitor measured variables is good, indicating a reliable data base.

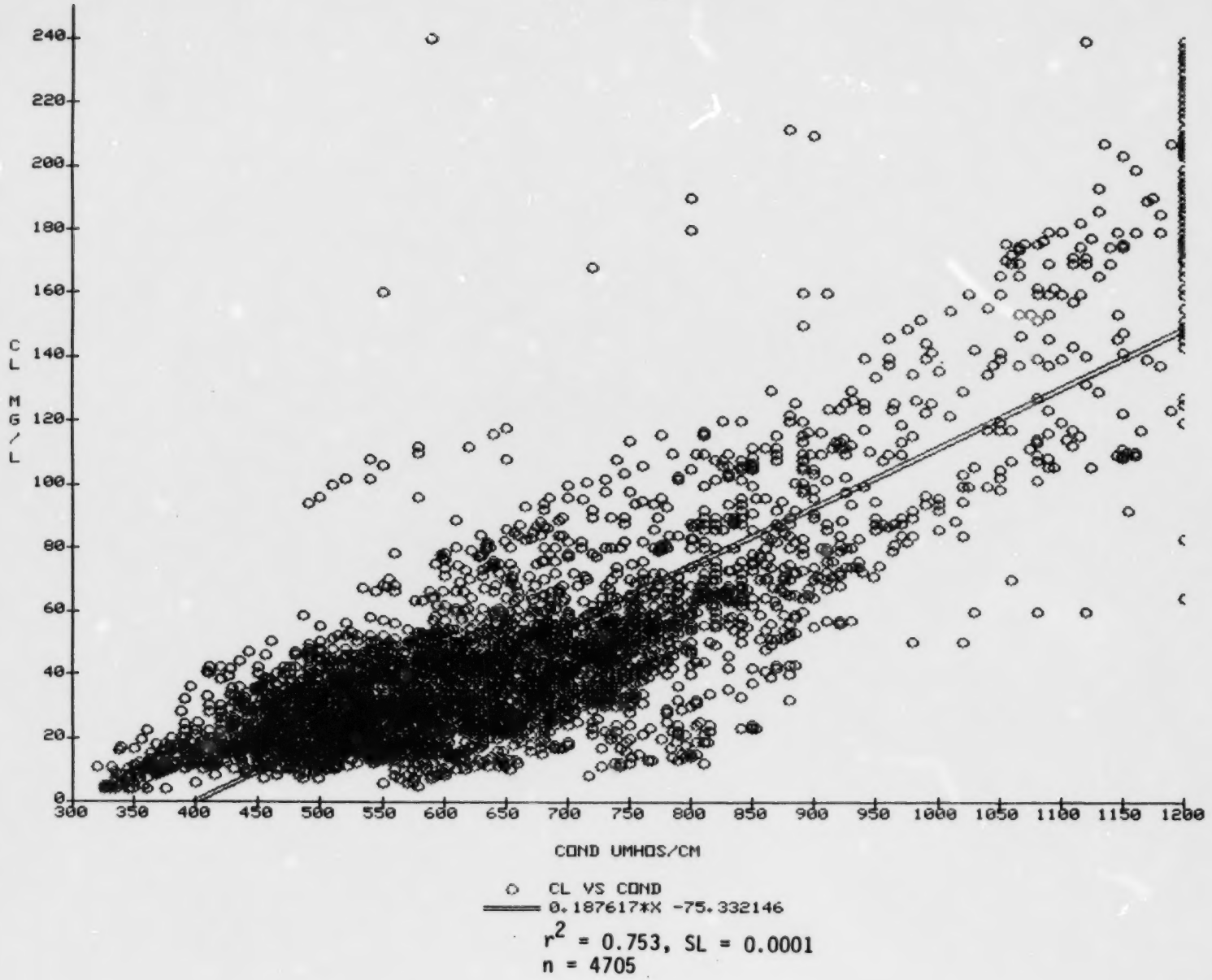



**Figure 7** Chloride vs Conductivity - Red River at Emerson, 1971-84.

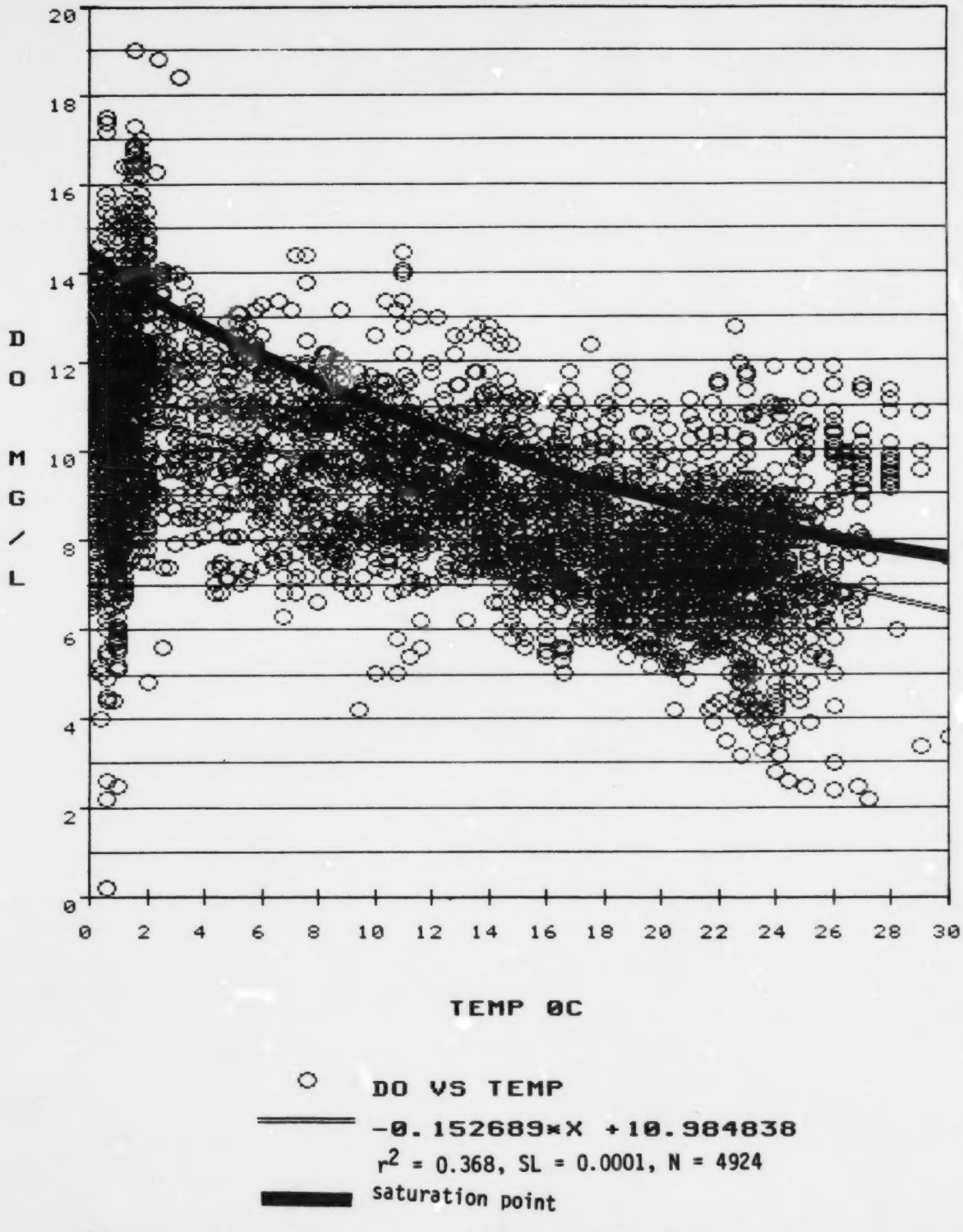



**Figure 8** D.O. vs Temperature - Red River at Emerson, 1971-84

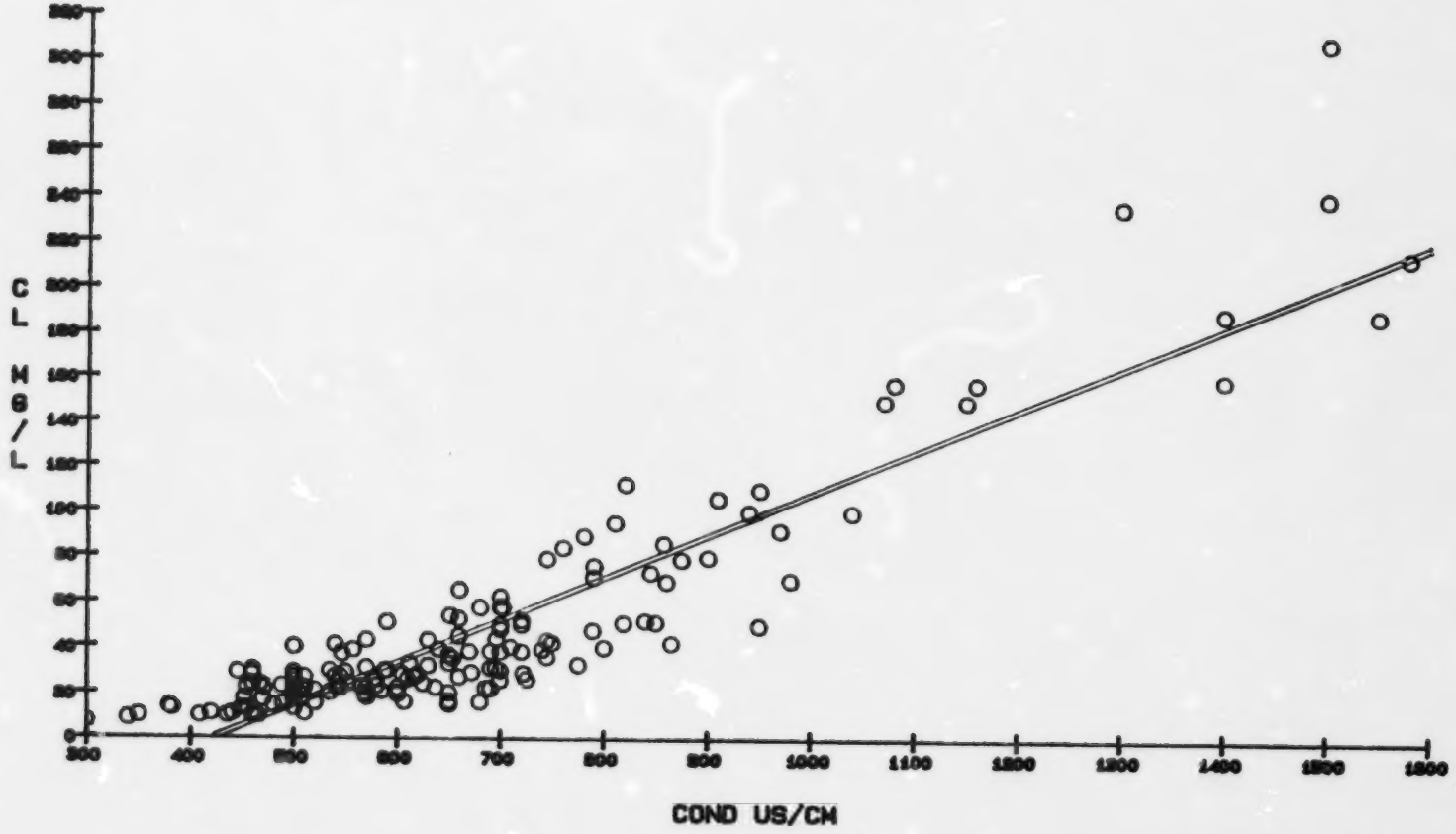



**Figure 9** Chloride vs Conductivity (Routine Grab) - Red River at Emerson, 1971-84

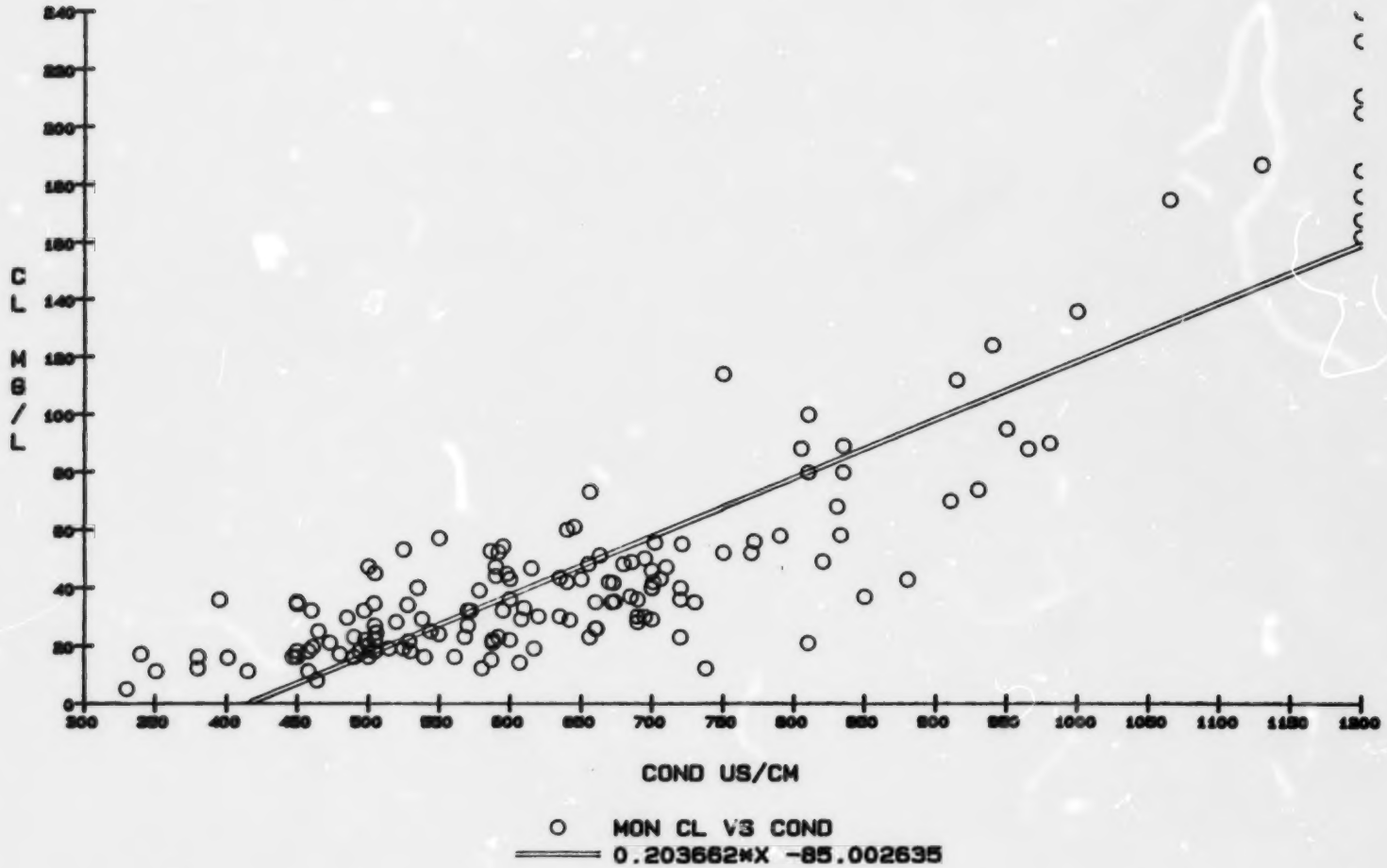



**Figure 10** Chloride vs Conductivity (Monitor) - Red River at Emerson, 1971-84.

4.1.c Monitor Data and Grab Sample Data

Statistical summaries of grab sample data and monitor data of corresponding days presented in Tables 2-b and 2-c, respectively, also reveal that generally the data distribution is skewed to the right, yielding higher means than median values. It is particularly evident for chloride and temperature. Data in these tables further reveal that the monitor values were somewhat lower for pH, DO and conductivity while they were higher for chloride and temperature. The higher monitor chloride values are believed to result from the poor sensitivity of the chloride probe at low concentrations while the higher temperatures probably reflect the effect of the heated water plant in which the monitor is housed. The effect of the heated water plant on DO is considered to be minimal since the Red River was generally undersaturated. The higher grab conductivity value at least in part is believed to result from a number of values above the 1200 uS/cm level, which was the upper limit of the monitor's range.

Correlations between the monitor data and the

routine grab sample data are presented in Figures 13-a,-b,-c,-d,-e. With coefficients of correlation ($r^2$) of 0.919, 0.905 and 0.980 for conductivity, chloride and temperature, respectively, the agreement for these variables is good. But for pH and possibly for DO, the correlations are poor ($r^2$ = 0.274 and 0.646, respectively).

As described in Sec. 2.2, water reaching the monitor had 0.5 to 3.5 hours of retention in a closed well. Therefore, at least in part, the above difference can be attributed to the real difference in these variables resulting from the cessation of photosynthetic activity while oxidation of organic matter continues lending to lower DO and pH.

In Sec. 3.0, it was also noted that the monitor values were daily means whereas the grab sample values were instantaneous day time values. Therefore, some differences in these data sets were expected, since a similar cessation of photosynthetic activity would occur at night. However, a comparision of the 1983-84 routine

sample data and the monitor data for three hours before and after the routine sample collection time also yielded similar correlations, suggesting more than the above noted causes for the observed differences. Since routine grab samples were not measured in situ but in a field lab, changes occurring during this short delay also cannot be ignored. Further investigation may be required to determine the exact causes of the observed differences between the monitor and the grab pH and DO.

### 4.1.d Total Dissolved Solids and Conductivity Ratios

Since conductivity is a function of the ionic concentration in water, conductivity measurements can be used in estimating the total dissolved solids (TDS). Similarly, TDS measurements can be used either to estimate or verify conductivity values. Regression plots in Figure 13-f show that the TDS:conductivity ratios for the routine sample and monitor are; $Y = 0.572 (X) + 11.525$ and $Y = 0.671 (X) - 44.670$, respectively. Based on these ratios, at mean and maximum levels the estimated TDS is within 5%. However, at lower concentrations the difference is about 15%. This observation along with supporting evidence seen in Figure 13-c, suggests that, as with chloride, the monitor conductivity values are somewhat higher at low concentrations. Despite these differences, the monitor TDS:conductivity agreement is good, again suggesting a sound data base.

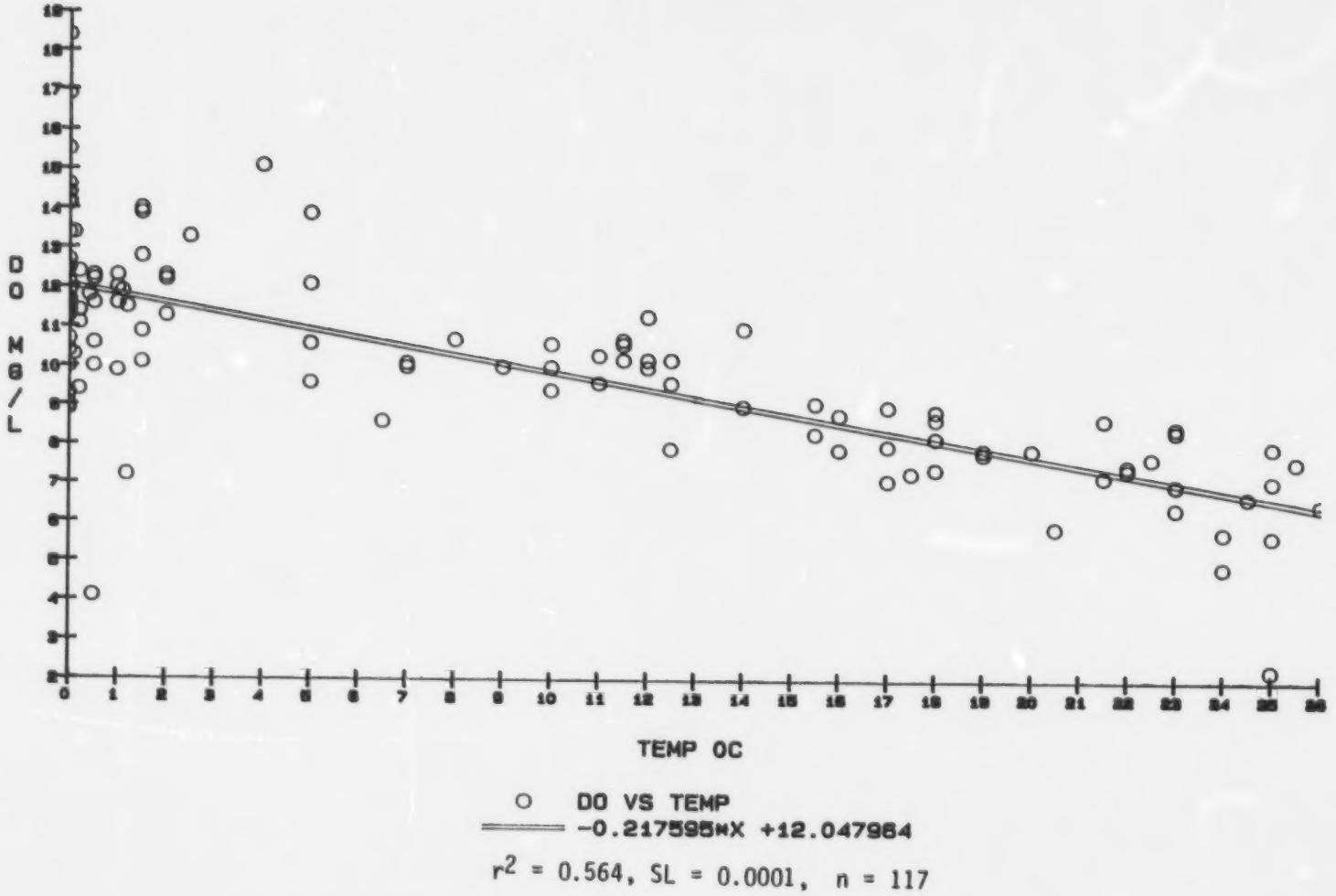



**Figure 11** DO vs Temperature (Routine Grab) - Red River at Emerson, 1971-84

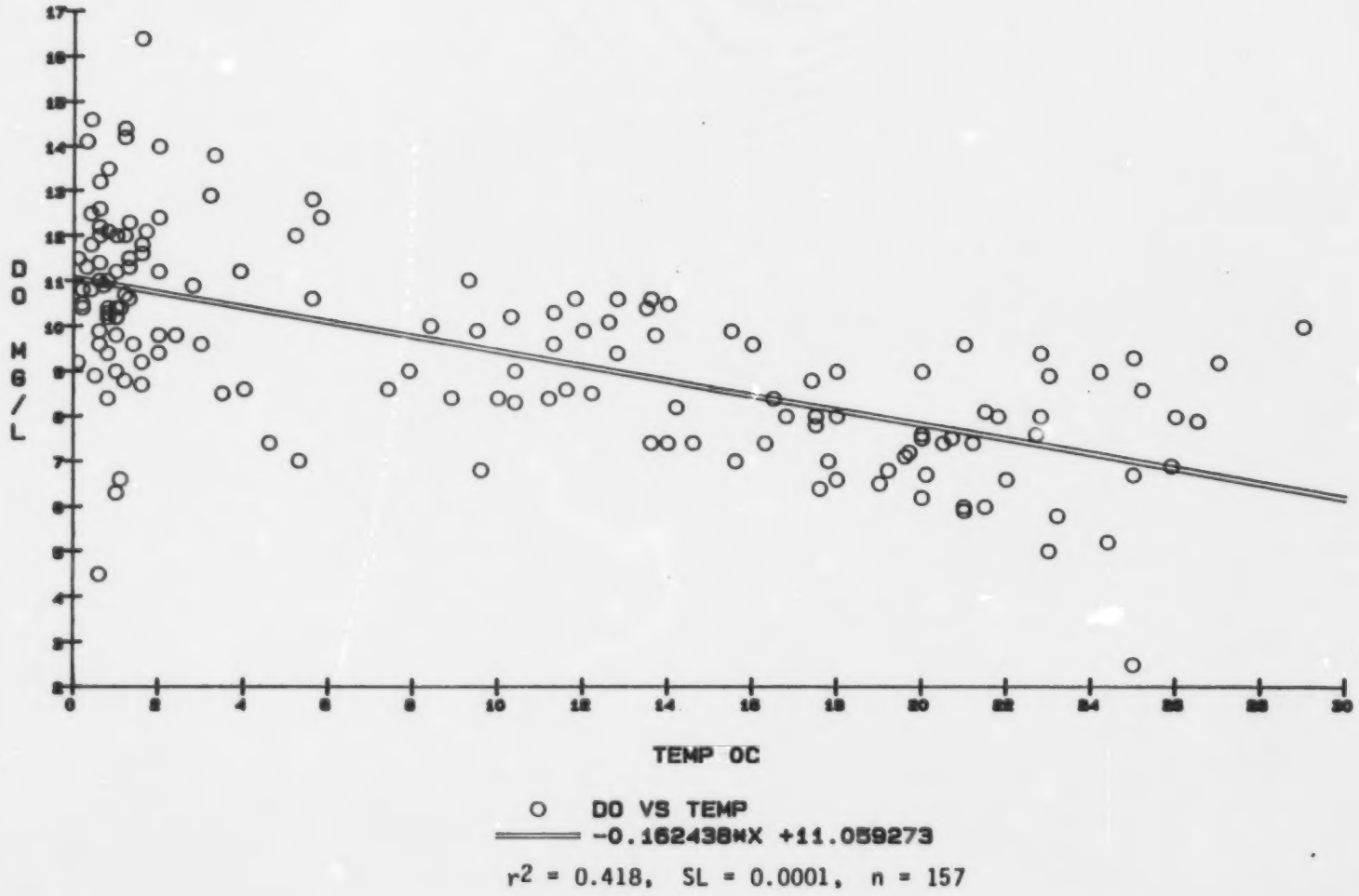



**Figure 12** DO vs Temperature (monitor) - Red River at Emerson, 1971-84.

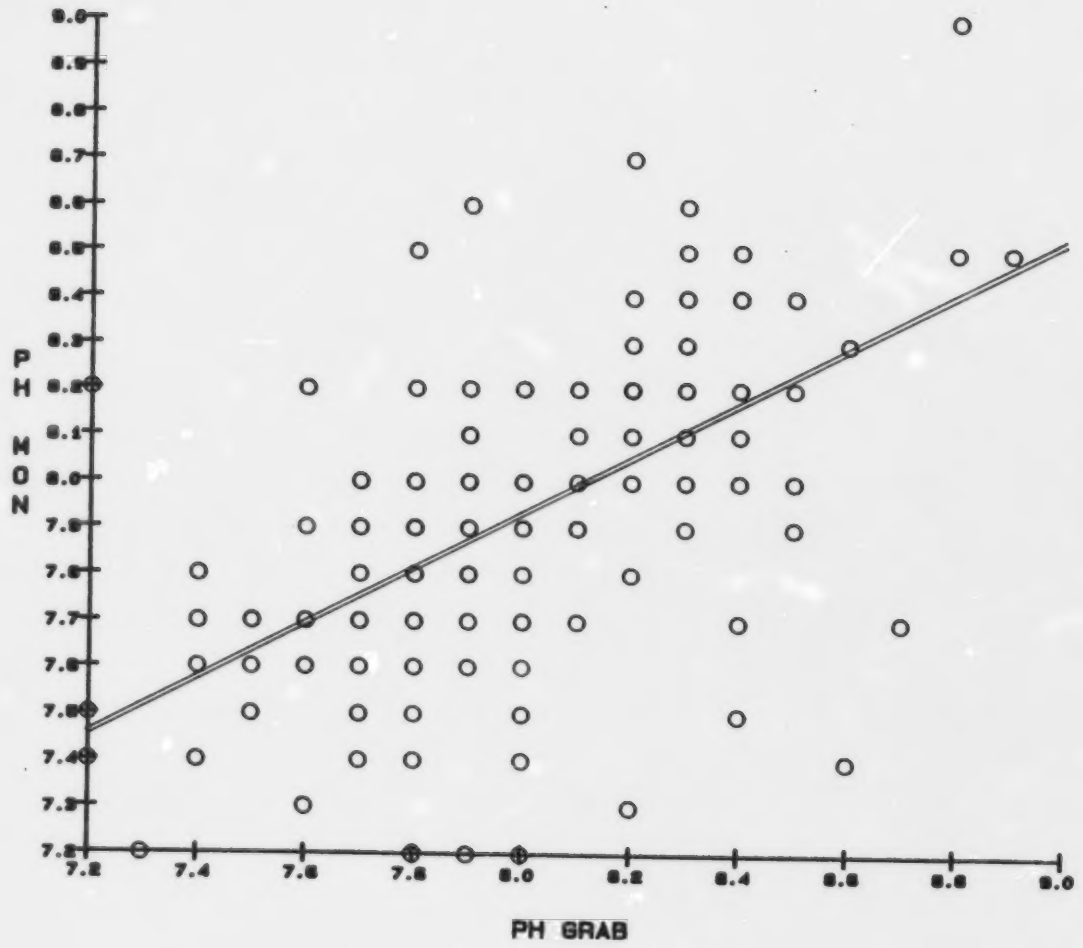



Figure 13a pH; Monitor vs Routine Grab - Red River at Emerson, 1971-84.

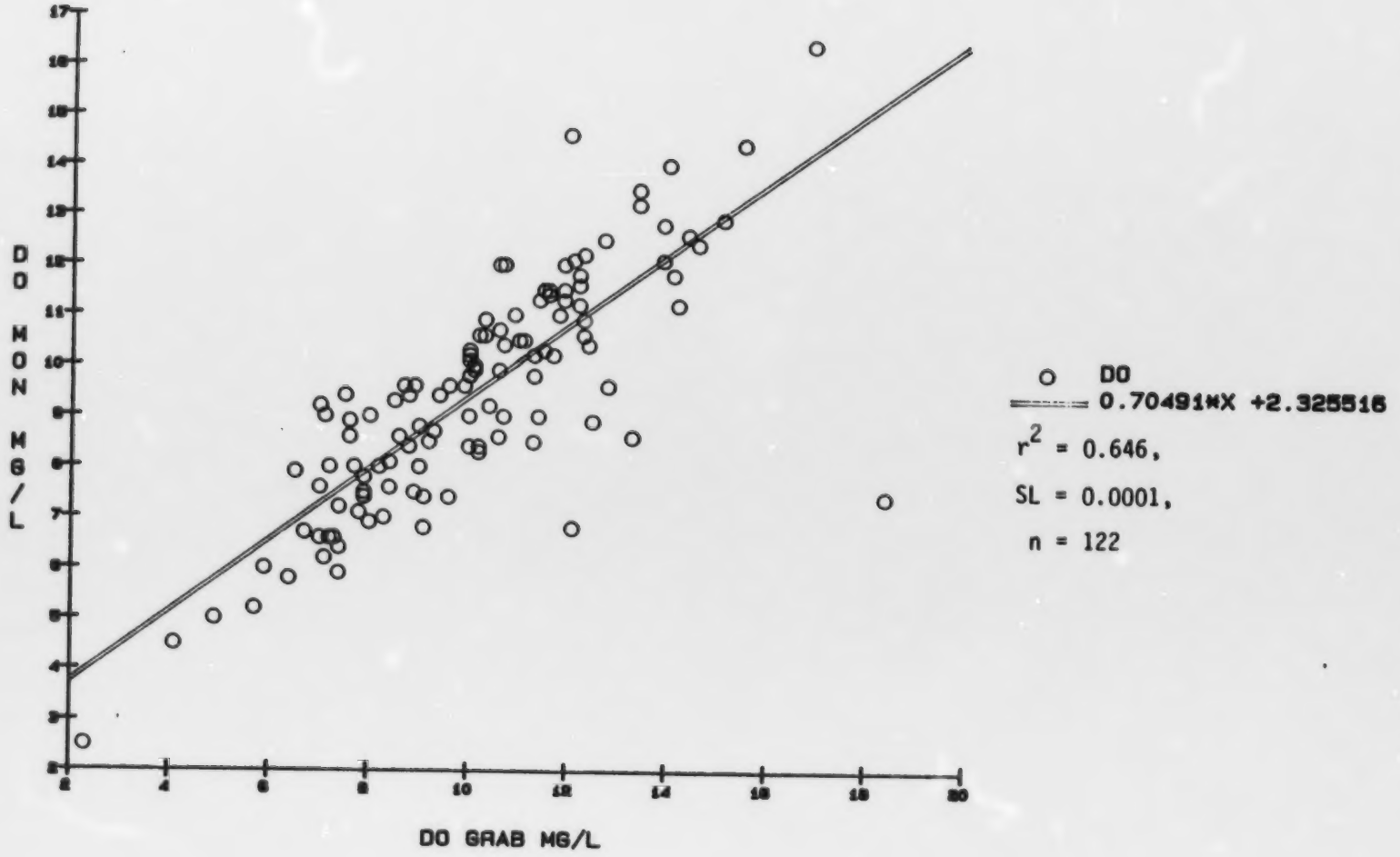



Figure 13b DO; Monitor vs Routine Grab - Red River at Emerson, 1971-84.

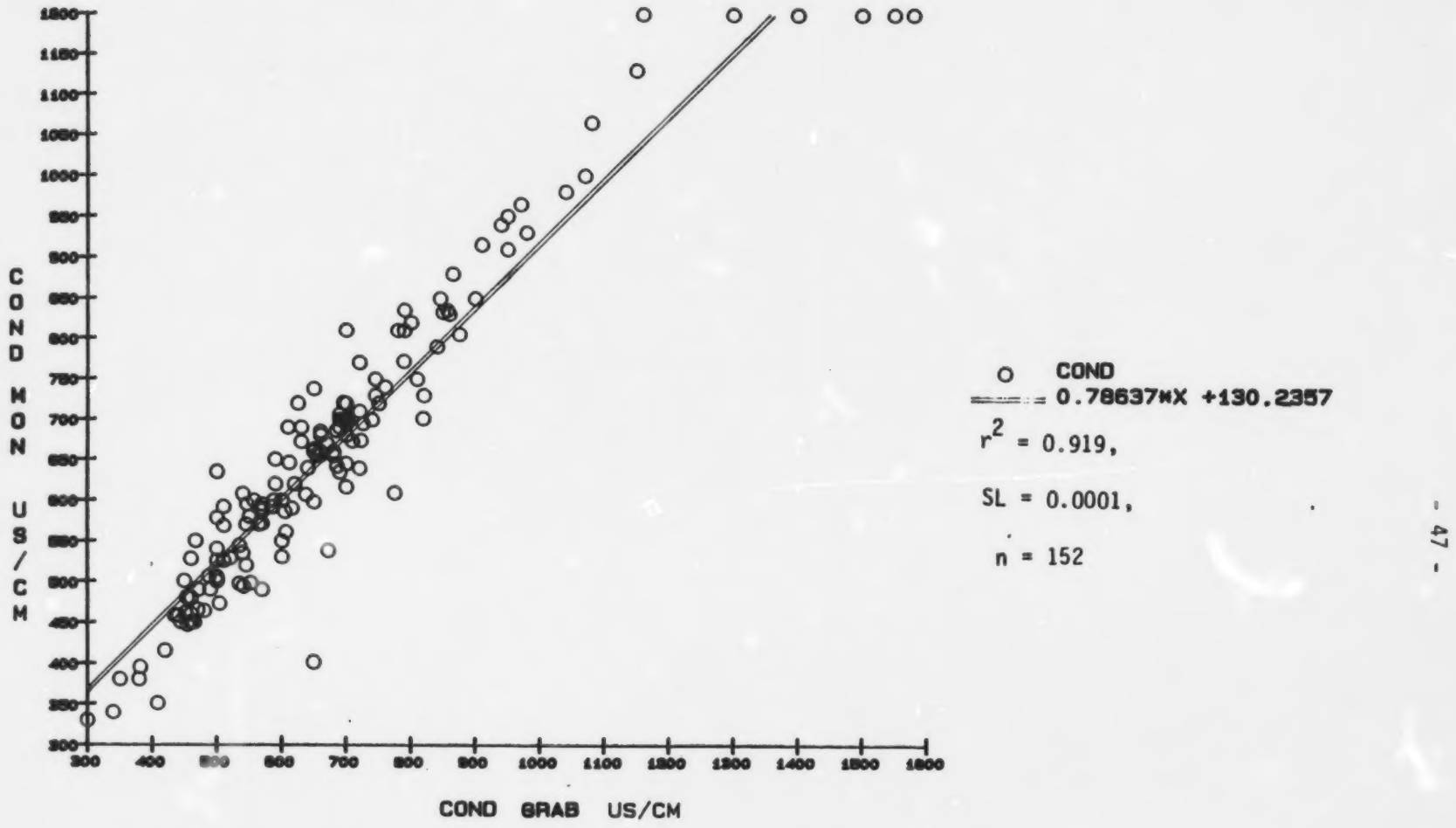



Figure 13c Conductivity; Monitor vs Routine Grab - Red River at Emerson, 1971-84.

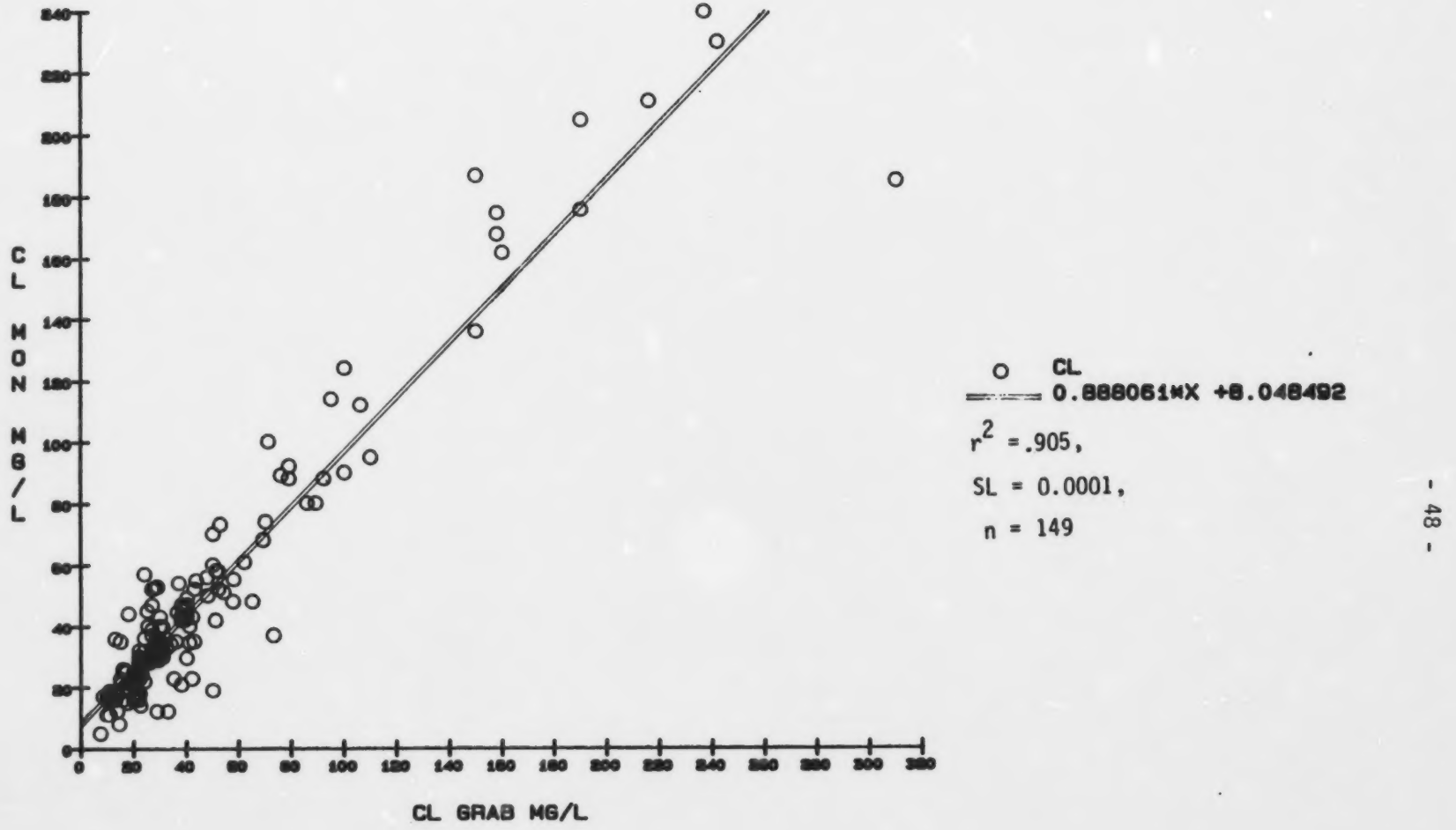



**Figure 13d** Chloride; Monitor vs Routine Grab - Red River at Emerson, 1971-84.

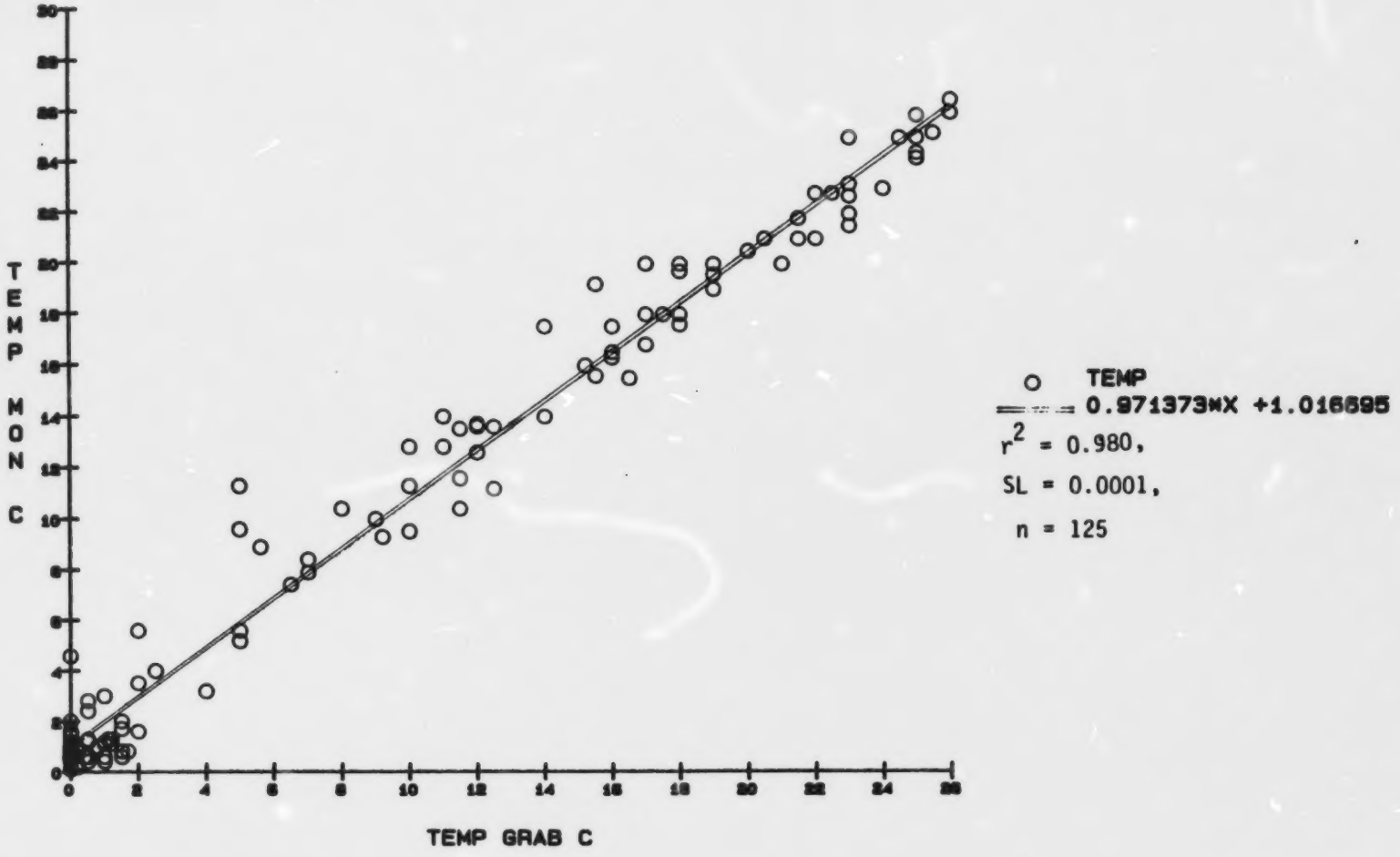



**Figure 13e** Temperature; Monitor vs Routine Grab - Red River at Emerson, 1971-84.

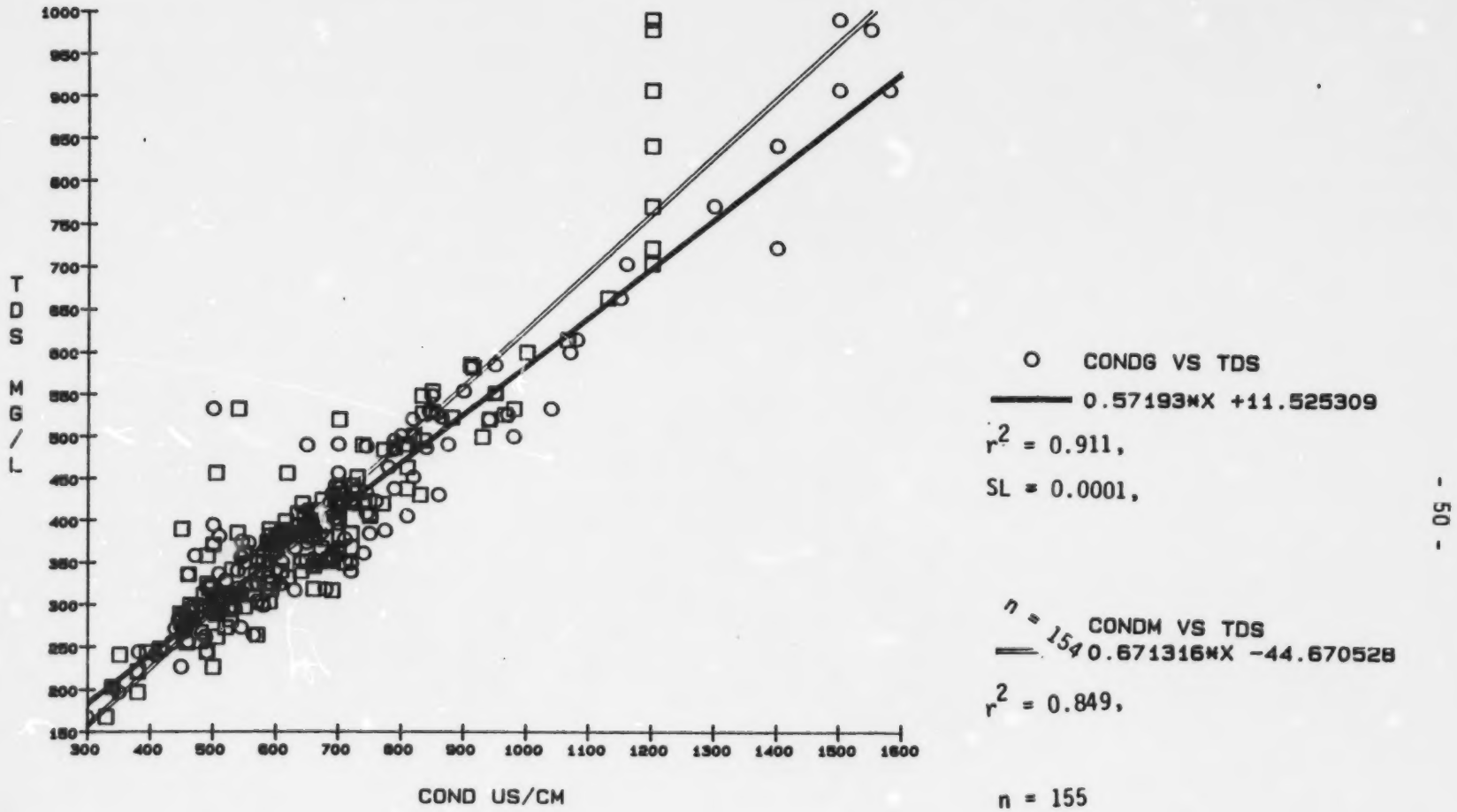



**Figure 13f** TDS vs Routine and Monitor Conductivity Values - Red River at Emerson, 1971-84

## 4.2 IJC Objectives and Exceedences

Data summary in Table 4 reveals that total dissolved solids (TDS) and chloride exceeded the IJC objectives approximately 10% of the time. Figures 6-c, 6-d show that most of these exceedences occurred during the winter period. Three years, 1977, 1980, 1981, when most of these exceedences occurred, were years with very low discharges (Figure 6-f). Therefore, it is evident that an important factor influencing the exceedences of TDS and chloride in the Red River is the discharge rate. During the last three years of this study, except for the 1984 TDS, neither the chloride nor TDS exceeded the IJC objectives. The reason for these relatively stable levels of TDS and chloride in recent years at least in part, appears to be related to high flow during the winter periods.

n = 154

Another important factor which may affect the TDS and chloride levels in the Red River is the discharge from Lake Ardoch, which has a chloride concentration exceeding 6000 mg/L (United States Environmental Protection Agency, 1977). An understanding reached between Canada and United

States in 1977 reduced the possibility of discharges from Lake Ardoch during the winter periods thus reducing the frequency of high TDS and chlorides in the Red River. The unusually large number of exceedences observed in 1977 (Table 4) were caused by the combined effect of a dry year and discharges from Lake Ardoch.

DO depression exceeded the IJC objective 1.4% of the days measured. In contrast to conductivity and chloride exceedences which usually occurred during the winter periods, the DO exceedences occurred either prior to the spring freshet or during the summer periods. The exceedences prior to the spring freshet, as records on file indicate, were related to sugar mill molasses discharges. The last of these molasses discharges detected was in 1979. The routine DO depletion during the summer period (Figures 5, 6-b) is attributed to the reduced solubility with higher temperature and to the rapid biological uptake during this period. Evidently, in the Red River, the negative effects of reduced solubility and bio-oxidation are greater than the positive effect of the photosynthetic activity. During the night

time when the photosynthesis is inactive, the temperature and biological uptake remain relatively high causing an even greater negative effect.

Since the low DO is a naturally occurring phenomenon in the Red River during the summer period, it stands to reason that discharges of any oxygen depleting wastes should be avoided during this period.

The IJC objective for pH was exceeded on 0.6% of the days measured, most frequently during the 1980-81 winter period. Except for two occasions in June 1975, the exceedences were above pH 9 levels. The two low values (below 6.5 pH) are doubtful values since records on file indicate a problem with the parameter probes at that time. As shown in Figure 6-a, the pH on several occasions was just under the pH 9 level and it is not known why it exceeded this level in 1980 and 1981.

IJC exceedences based on the routine grab samples are given in Table 5. It is noteworthy that the

routine monthly samples revealed a similar percentage of exceedences to that shown by the monitor. However, monthly samples did not reveal either the duration or the severity of each exceedence, which are essential in assessing the biological impact. For example, in 1979 a sugar mill molasses discharge resulted in an oxygen sag of 6 days, which included a thirty-four hour period of below 1.0 mg/L DO and a fish kill. Although the routine sampling detected a low DO of 4.1 mg/L during this period, it was totally deficient in assessing the impact of this severe event. Therefore, to detect and assess the exceedences of the IJC objectives and, as discussed in Section 4.3.2, to detect any long term trend, the maintenance of a continuous monitor is essential.

TABLE 4. Yearly Exceedences of IJC Objectives in Days

| Year | pH | DO | Cond.(1) | Cl. |
|---|---|---|---|---|
| 1971 | 2 | 3 | 2 | 0 |
| 1972 | 0 | 0 | 6 | 6 |
| 1973 | 0 | 0 | 12 | 9 |
| 1974 | 0 | 0 | 8 | 6 |
| 1975 | 2 | 33 | 6 | 5 |
| 1976 | 0 | 0 | 43 | 47 |
| 1977 | 0 | 1 | 204 | 175 |
| 1978 | 0 | 0 | 44 | 10 |
| 1979 | 1 | 10 | 34 | 7 |
| 1980 | 14 | 3 | 113 | 98 |
| 1981 | 9 | 17 | 107 | 69 |
| 1982 | 0 | 0 | 0 | 0 |
| 1983 | 0 | 0 | 0 | 0 |
| 1984 | 0 | 2 | 18 | 0 |
| Total Days of Exceedence | 28 | 69 | 597 | 432 |
| Total Days Monitored | 4935 | 4925 | 4949 | 4706 |
| Exceedence in % | 0.6 | 1.4 | 12.1 | 9.2 |
| IJC Objective | 6.5-9.0 (2) | 5.0 mg/L | 855-uS/cm | 100-mg/L |

(1) Conductivity value for 500 mg/L TDS; computed from the best regression fit $x = \frac{y-11.53}{0.572}$

(2) IJC proposed range

TABLE 5. IJC Exceedences Based on Routine Grab Sampling

| Parameters | IJC Objectives | Number of Observations | Number of Exceedences | Exceedences in % |
|---|---|---|---|---|
| pH units | 6.5 - 9.0 | 162 | None | N.A. |
| DO mg/L | 5.0 | 126 | 3 | 2.4 |
| Cond. uS/cm | 855 | 157 | 23 | 14.7 |
| Cl mg/L | 100 | 162 | 14 | 8.6 |

## 4.3 Seasonal and Long-term Trends in Water Quality

### 4.3.1 Seasonal Trend

#### 4.3.1.a pH

The mean monthly pH values for the 1971-84 study period are presented in Figure 5. The range of these mean monthly values was 0.56, with minimums occurring in February and March and maximum in November. The lower winter values probably reflect the effect of the reduced photosynthesis during this period and the contributions of ground water with a pH of 7.5 (Cherron 1969). The higher values in the late fall suggest the continuation of photosynthesis during this period. Maximum fluctuations in June and July (Table 6) suggest varying rates of biological activity during this period, but the diurnal fluctuations were not as distinct as those observed in the Souris River (Munro and Crosley, 1984). As discussed in Sec. 4.1.c, the limited diurnal fluctuations are believed to be related to the retention of water in a closed dark well prior to reaching the monitor.

4.3.1.b DO

The mean monthly DO values are given in Figure 5. As expected, the lowest DO values were observed during the summer, when the water temperature is the highest and biological uptake is at a peak. Despite the effluent spills that have periodically occurred prior to the spring freshet, the overall DO level during the spring was relatively high. The DO profile in Figure 5 shows that the Red River is not oxygen deficient during the winter period, and unless it is an unusual event, low DO levels are expected only during the summer period. DO peaked in late fall, which suggests the continuation of algal photosynthesis while overall microbial respiration is at a reduced rate.

As seen in Figure 8 the DO was inversely related to the temperature but this relationship was poor, yielding a $r^2$ value of only 0.368. The saturation curve in Figure 8 also indicates that the Red River was generally undersaturated, particularly in the 2°C to 8°C region where the spring runoff occurs. This probably reflects the effect of biodegradable substances transported

during this period. As with pH, the diurnal fluctuations were not as distinct as they were in the Souris River.

4.3.1.c Conductivity

Conductivity was lowest during the spring freshet (Figure 5), clearly indicating the diluting effect of the snow melt water. As indicated in Sec. 4.3.1.a, the increased conductivity during the winter is attributed mainly to the effects of ground water discharge. In his study, Charron (1969) observed that generally the ground water in the Red River basin is saturated with calcium carbonate and has varying concentrations of chloride and sulphate. The proportion of these hard waters in surface water tends to be greatest under winter low flow conditions. Not only were the winter conductivities higher than those during other periods, but the fluctuations also were at a maximum during this period (Table 6). Possible explanations for this substantial fluctuation include incidents of snow-melt, the varying amount of ground water discharge during the winter period and, until 1977, discharges from Lake Ardoch. The

decrease in concentrations observed in the fall is attributed to fall rains causing increased discharge and dilution during this period.

As shown in Figure 14, the conductivity in the Red River is inversely related to the discharge, but with a linear correlation coefficient ($r^2$) of 0.118 , this relationship was poor, probably reflecting the variations observed at extreme flow conditions. This observation is consistent with the findings reported by HydroQual Consultants Inc. (1986). The correlation is only slightly improved by transferring data into a log format ($r^2$ = 0.325).

4.3.1.d Chloride

The annual pattern of chloride concentrations resembles that for conductivity, having low concentrations during the spring and high during the winter period. But, it does not have the same pronounced dilution effect during the spring freshet (Figure 5). The relatively high concentration of chloride observed during the spring freshet is believed to result from the use of salt on the roads during the winter.

The correlation between chloride and discharge was even poorer than that between conductivity and discharge (Figure 15), again suggesting wide variations at flow extremes. As with conductivity, higher concentrations during the winter period can be attributed to ground water discharge and, prior to 1978 discharges from Lake Ardoch.

Data in Table 6 also reveal that the chloride fluctuation in the Red River is substantial, yielding standard deviations (2s) larger than the mean values. With such large fluctuations, a reliable prediction of the chloride concentration in the Red River is difficult.

4.3.1.e Temperature

The mean monthly temperature in the Red River varied from 0.76$^{o}$C to 23.26$^{o}$C, following the characteristic annual bell shaped curve. As indicated in Sec. 4.3.1.b, temperature greatly affects the DO concentration. The lowest mean monthly DO was observed with the maximum temperature in July.

Table 6 Mean Monthly Concentration - Red River at Emerson, 1971 - 1984

(± 2s Given in Parentheses)

| MONTH | pH (pH units) | DO (mg/L) | COND (uS/cm) | Cl (mg/L) | T (°C) |
|---|---|---|---|---|---|
| January | 7.69 (0.41) | 10.79 (2.73) | 687.4 (393.0) | 52.7 (91.0) | 0.93 (1.04) |
| February | 7.64 (0.47) | 10.41 (2.79) | 661.0 (388.5) | 46.5 (88.6) | 0.76 (0.82) |
| March | 7.64 (0.52) | 9.68 (2.86) | 619.7 (242.9) | 39.7 (51.3) | 0.99 (1.27) |
| April | 7.73 (0.55) | 9.64 (3.02) | 570.9 (265.5) | 37.1 (61.6) | 5.61 (4.67) |
| May | 7.89 (0.54) | 8.35 (1.52) | 650.5 (221.1) | 36.1 (38.1) | 14.61 (4.15) |
| June | 7.86 (0.56) | 7.49 (1.59) | 682.5 (213.2) | 39.9 (60.5) | 19.68 (3.12) |
| July | 7.83 (0.66) | 7.34 (2.94) | 626.9 (258.2) | 42.9 (69.7) | 23.26 (2.96) |
| August | 8.01 (0.51) | 7.59 (2.08) | 625.6 (290.6) | 46.5 (76.8) | 22.36 (3.68) |
| September | 8.05 (0.46) | 8.65 (1.79) | 605.5 (274.3) | 49.9 (60.8) | 16.27 (2.97) |
| October | 8.08 (0.39) | 9.79 (2.01) | 643.1 (389.0) | 50.3 (78.9) | 9.28 (3.23) |
| November | 8.20 (0.43) | 11.65 (2.91) | 721.4 (363.5) | 62.2 (76.7) | 2.68 (2.45) |
| December | 8.01 (0.51) | 11.91 (2.99) | 804.3 (386.1) | 74.5 (99.0) | 0.98 (1.26) |

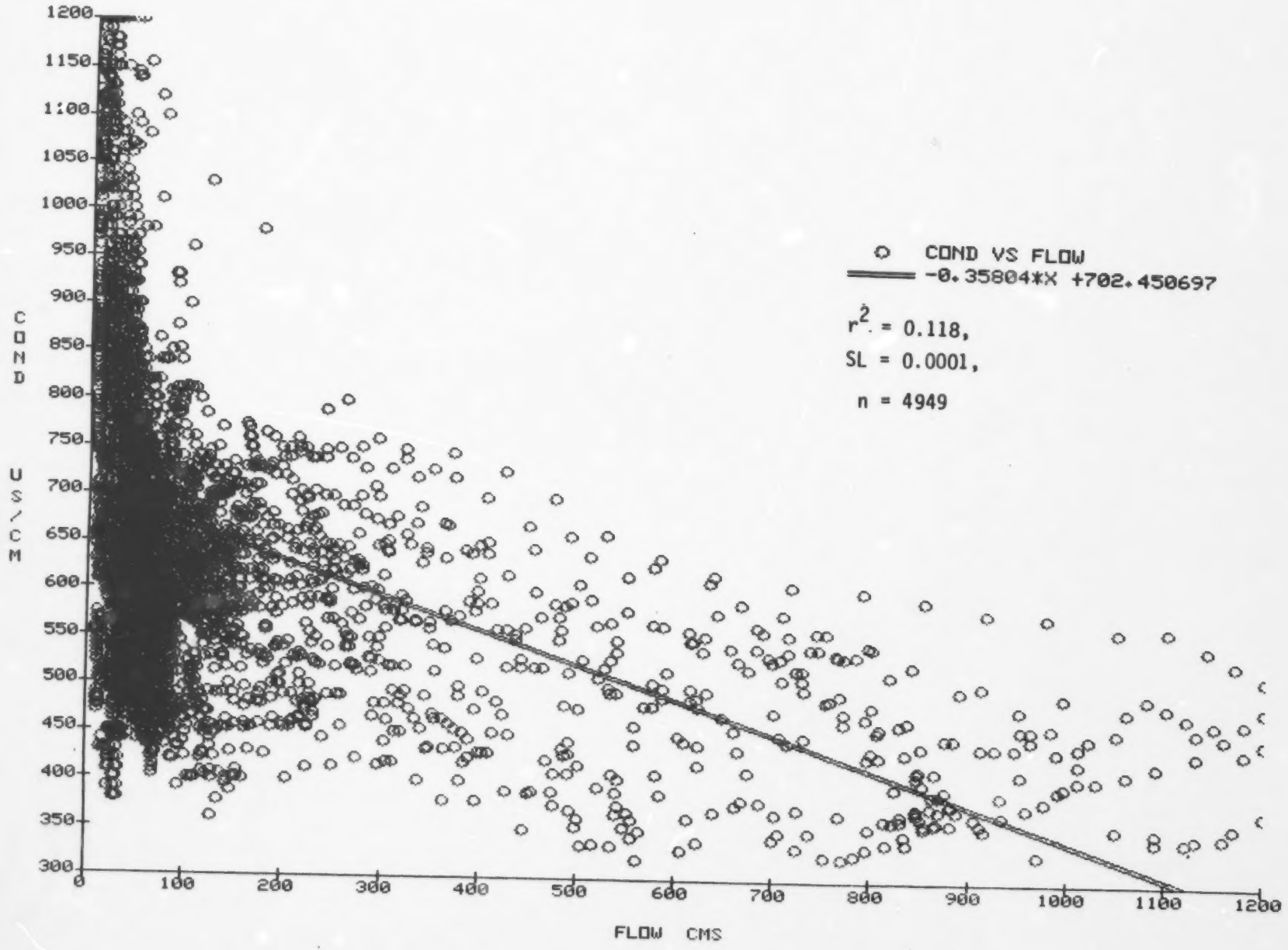



**Figure 14** Conductivity vs Discharge - Red River at Emerson, 1971-84.

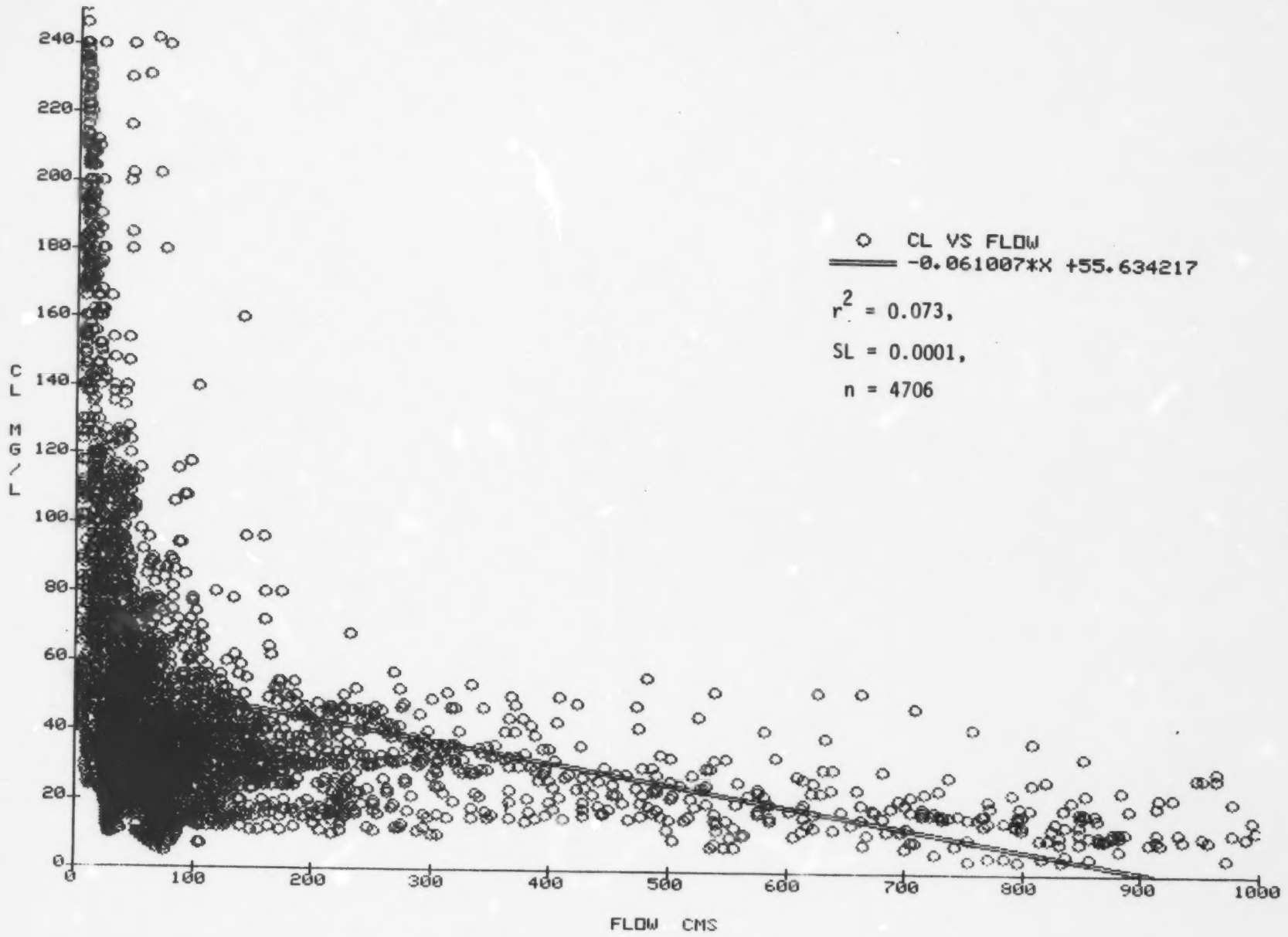





**Figure 15** Chloride vs Discharge - Red River at Emerson, 1971-84.

### 4.3.2 Long-term Trends

Linear regression analysis of the routine monthly data did not reveal any significant trends (levels of significance = 0.05). However, with the exception of temperature, the monitor data showed significant trends and these are dealt with in the following sections.

#### 4.3.2.a pH

The mean pH of the 1971-84 study period was 7.89, with a daily minimum of 6.20 and maximum of 9.50 (Table 2-a). As noted in Sec. 4.2, the low 6.20 pH value is questionable, but the maximum values, occurring mostly during the late fall of 1980, are considered to be correct since the routine grab samples also yielded similar high values during this period. Since the DO remained relatively high during this period, no waste discharge is suspected of causing this high pH. A probable cause is the continuation of photosynthesis during this period of unusually high fall and winter temperatures (Figure 6-e).

Since 1982, the monthly extremes have become noticeably narrower. This phenomenon is observed for conductivity and chloride as well. In the case of conductivity and chloride, as discussed in Sec. 4.2, the reason is believed to be the relatively higher river discharge during the winter and the absence of discharges from Lake Ardoch. But for pH, the maximum monthly extremes were observed during the summer periods and it is not known why they have become narrower since 1982.

Maximum monthly extremes of the 1971-84 study period were observed between 1976 and 1981. This is consistent with the maximum monthly extremes observed for discharge and other variables, suggesting a natural phenomenon in the Red River (Figures 6-a, b,c, d, e)

An increasing trend in monthly mean pH evident in Figure 6-a is further substantiated by the linear regression results in Figure 16-a. In an earlier report Guilbault (1981) observed an increase in pH during 1971-77 and a detailed statistical analysis of the 1971-84 data by the HydroQual Consultants Inc. (1986) also confirmed an increase in pH from

1981 onwards. This overall increasing trend in pH could have been accepted as an indication of improving water quality in the Red River except that it appears to coincide with a decrease in DO. A probable cause of the increasing trend in pH is the increasing algal activity in the Red River. Data on file suggest an increasing chlorophyll-a concentration in the Red River, which was the likely cause of this pH increase.

4.3.2.b DO

The mean DO of the 1971-84 study period was 9.49 mg/L, with daily minimum of 0.2 and maximum of 18.80 mg/L (Table 2-a). As indicated in Sec. 4.2, the low values occurred either when there was a sugar mill molasses discharge or during warm summer periods. Pronounced effects of the sugar mill molasses discharges are seen in 1975 and 1979 (Figure 6.b). As discussed in Sec. 4.3.2.a, the monthly extremes have become narrower since 1982.

Linear regression results in Figure 16-b reveal that the DO content of the Red River had a very small but statistically significant decrease.

This observation is consistent with the observed increase in algal content. A detailed analysis of the data by HydroQual Consultants Inc. (1986) showed that the DO actually increased from 1974-77, decreased from 1978-81 and again recovered from 1982 onwards. Therefore, although the DO decrease was statistically significant for the entire period, the decrease was mostly confined to the 1978-81 period.

4.3.2.c Conductivity

The mean conductivity for the 1971-84 study period was 663.07 uS/cm, with a daily minimum of 320 and maximum of 2000 uS/cm. As indicated in Sec. 4.2 and 4.3.1.c, the minimums occurred during the spring freshets and the maximums during the winter periods, particularly during the winter periods of dry years. Despite such a seasonal pattern, the conductivity varied substantially from year to year with no clear pattern (Figure 6-c; Table 7). Nevertheless, linear regression in Figure 16-c clearly indicates a significant increase and this increase appears to have been greatly influenced by the high conductivity of the 1976-81 dry

period. Data from 1982 on do not indicate an increase.

4.3.2.d Chloride

The mean chloride concentration of the 1971-84 study period was 48.82 mg/L, with daily minimum of 4.00 and maximum of 437.00 mg/L. The chloride minimum and maximum followed the conductivity concentration profile (Figure 6-d). As with conductivity, very high concentration values were observed during the dry years of 1977, 80, 81, but for chloride the ratio of concentration also increased during these dry years (Table 7), suggesting proportionally higher chloride in ground water. These observations suggest that dry years are more critical in terms of high chloride occurrences than the high TDS occurrences.

As seen in Figure 6-d, and confirmed by the large standard deviations of mean monthly values in Table 6, the year to year variation in chloride concentration was substantial. The period of low monthly extremes observed from 1982 on is longer than earlier periods (1970-71, 1974-75, 1979-80),

but more years of data are needed before a trend can be confirmed.

Analogous to conductivity, the apparent upward trend in chloride concentration (Figure 16-d), was also influenced by the unusually high concentrations during the 1976-81 dry period.

4.3.2.e Temperature

As expected the water temperature varied widely between the seasons (Figure 6-e), but with minimal variation between years. The mean temperature of the Red River during the 1971-84 study period was 9.76$^{o}$C. Except for the unusually high temperatures observed in 1971, no unusual deviation was observed.

Linear regression results in Figure 16-e suggest a small decrease in temperature, but more years of data are needed before any such trend could be confirmed.

Table 7 Conductivity:TDS, Conductivity:Chloride and TDS:Chloride Ratios - Red River at Emerson

| Year | Conductivity: TDS | Conductivity: Chloride | TDS: Chloride | Conductivity: uS/cm |
|---|---|---|---|---|
| 1971 | 1:0.75 | 25:1 | 19:1 | 591 |
| 1972 | 1:0.60 | 21:1 | 12:1 | 557 |
| 1973 | 1:0.63 | 14:1 | 9:1 | 646 |
| 1974 | 1:0.69 | 18:1 | 12:1 | 568 |
| 1975 | 1:0.58 | 19:1 | 11:1 | 557 |
| 1976 | 1:0.57 | 13:1 | 8:1 | 663 |
| 1977 | 1:0.62 | 9:1 | 5:1 | 914 |
| 1978 | 1:0.58 | 17:1 | 10:1 | 701 |
| 1979 | 1:0.52 | 15:1 | 8:1 | 710 |
| 1980 | 1:0.54 | 10:1 | 5:1 | 820 |
| 1981 | 1:0.60 | 7:1 | 4:1 | 809 |
| 1982 | 1:0.64 | 15:1 | 10:1 | 523 |
| 1983 | 1:0.59 | 13:1 | 8:1 | 616 |
| 1984 | 1:0.55 | 17:1 | 9:1 | 613 |
| Mean | 1:0.60 | 15:1 | 9:1 | 663 |

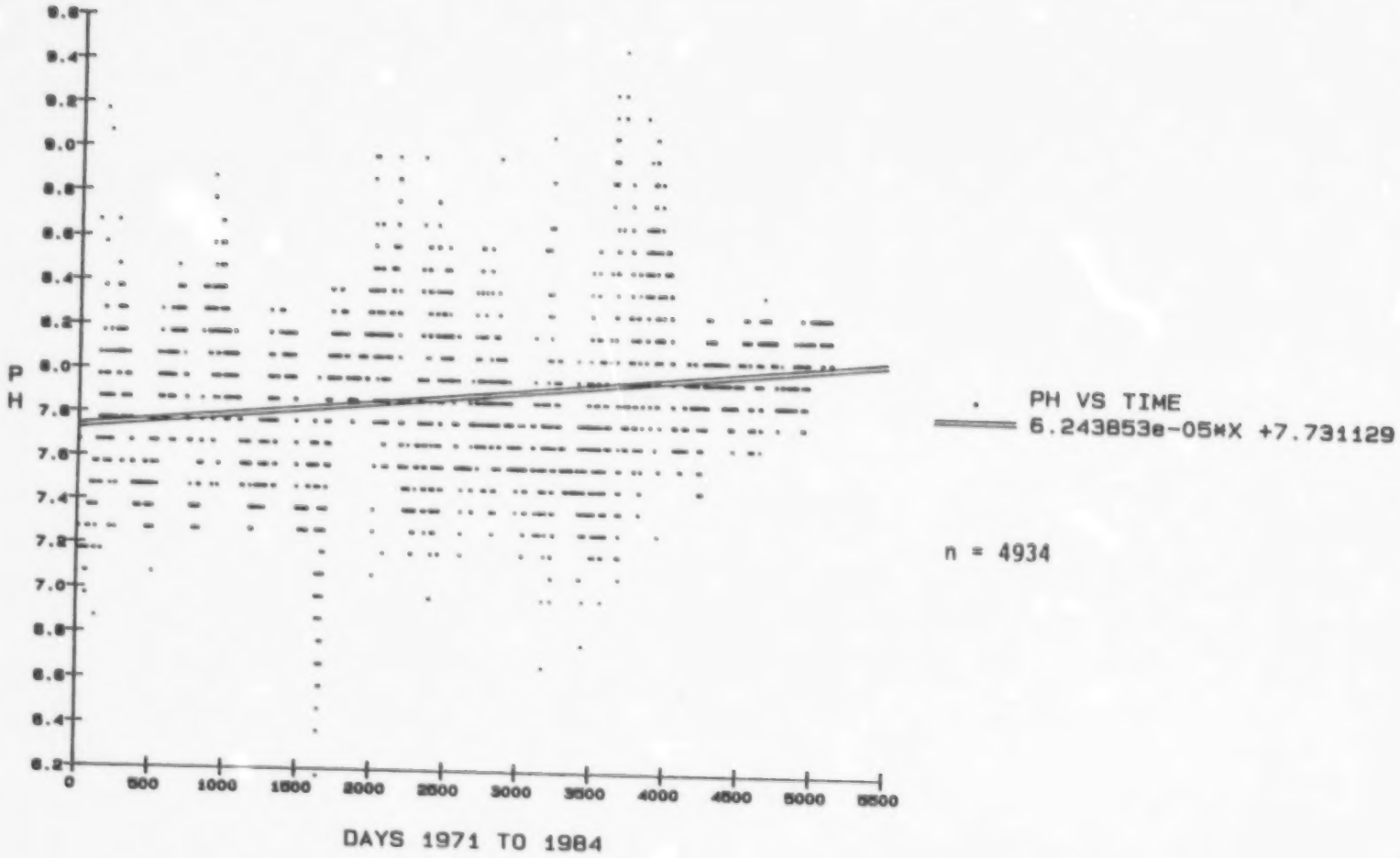



**Figure 16a** Linear Regression Plot - pH

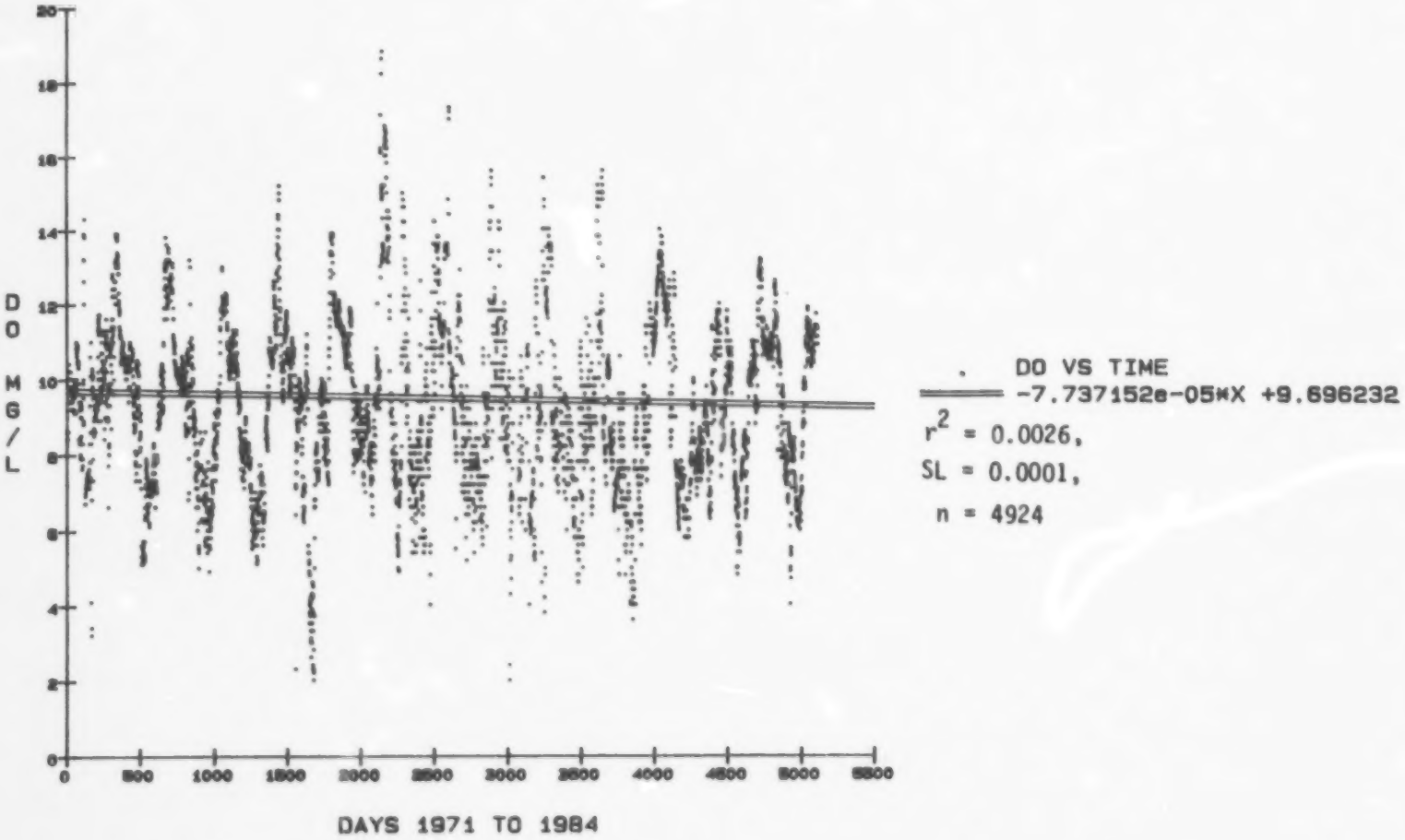



**Figure 16b** Linear Regression Plot - DO

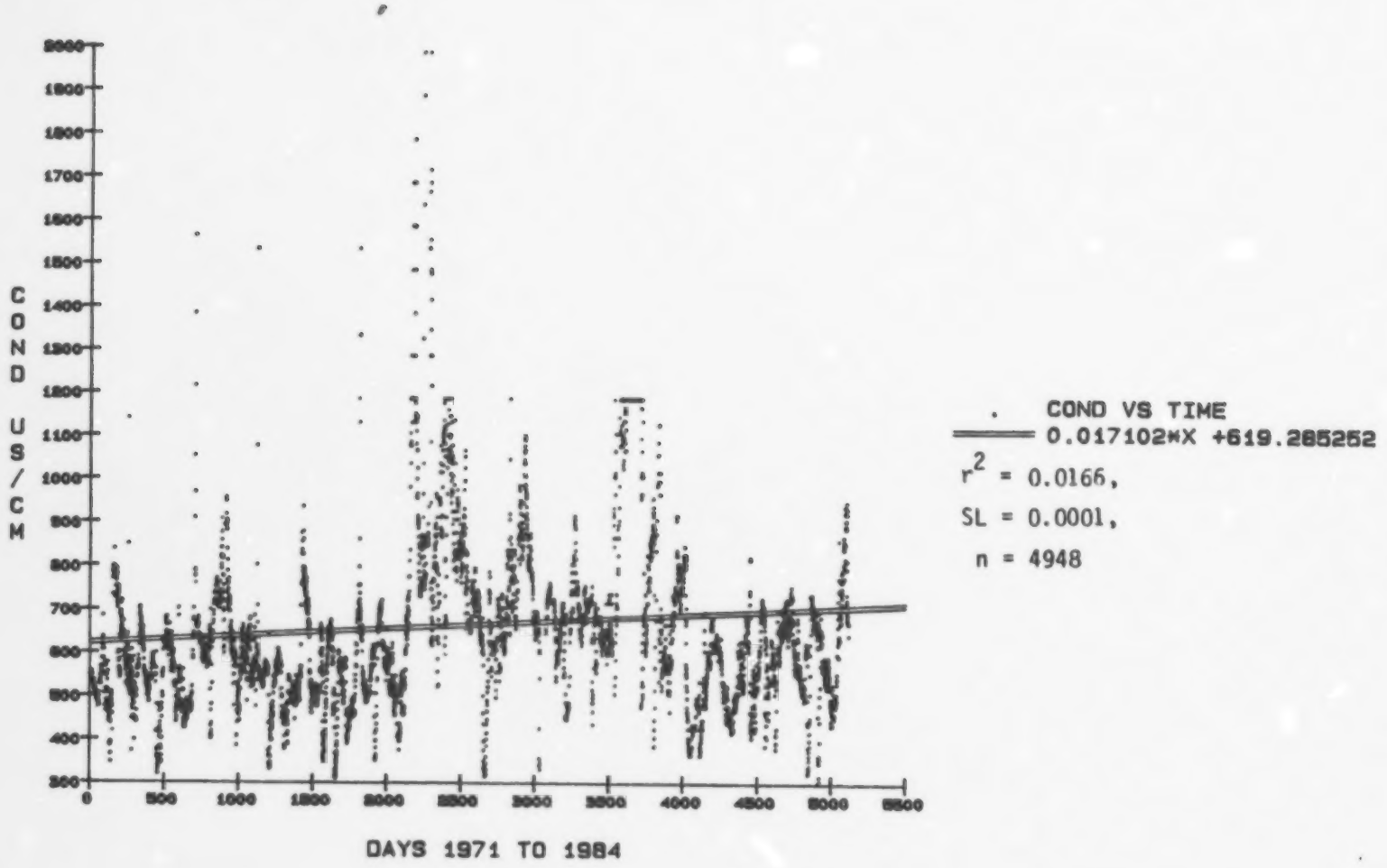



Figure 16c Linear Regression Plot - Conductivity

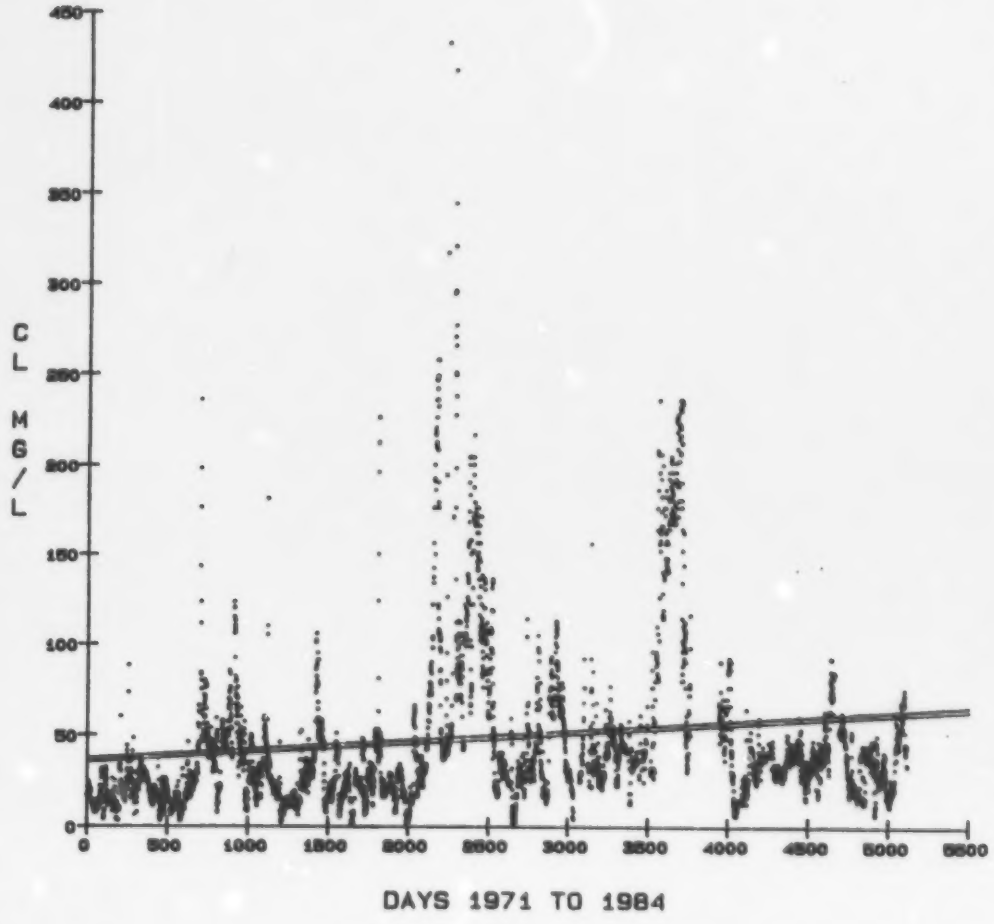
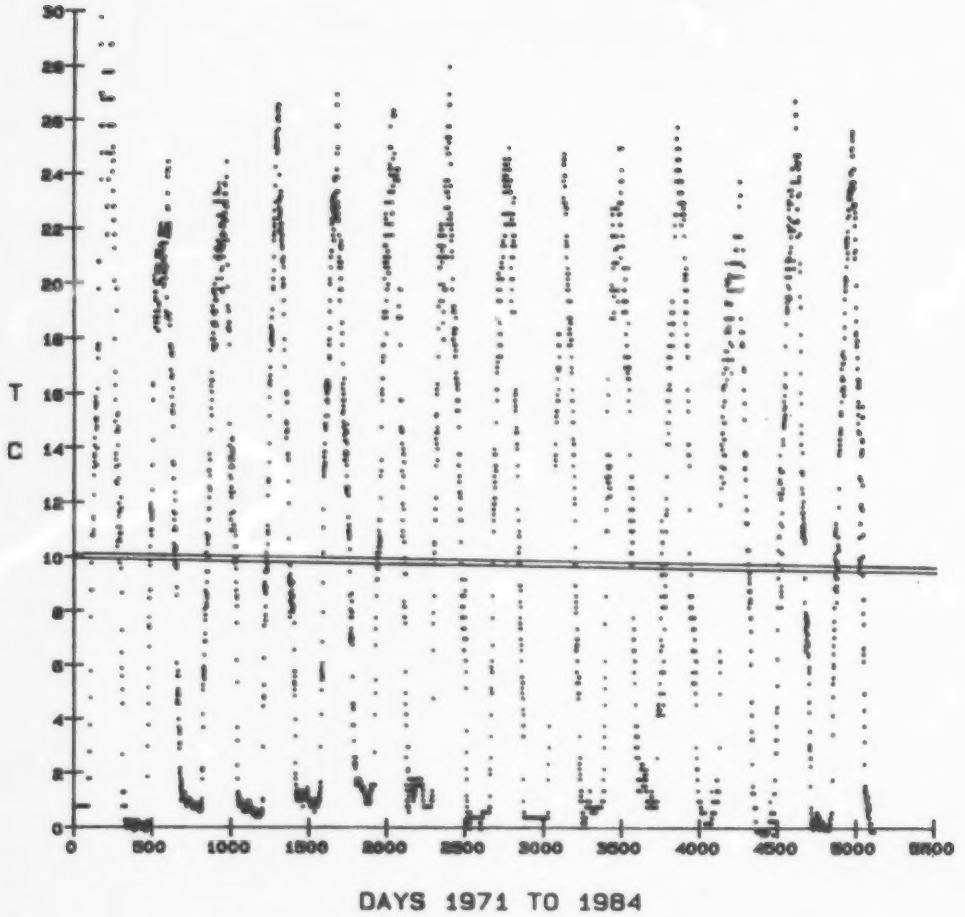



Figure 16d Linear Regression Plot - Chloride




TEMP VS TIME
-9.364344e-05*X +10.006211
$r^2$ = 0.0002,
SL = 0.276,
n = 4948

**Figure 16e** Linear Regression Plot - Temperature

# 5.0 CONCLUSIONS AND RECOMMENDATIONS

With the exception of chloride, the data recovery was virtually complete. Data loss associated with monitor failure was about 2%.

Based on the calibration protocol, intra-relation of the monitor data and the agreement between the monitor and the routine grab samples, it is concluded that generally the monitor generated data are of sound quality. The cause of the comparatively poor agreement observed for the pH, and to a lesser extent for DO, is believed to result from a combination of factors such as the retention of water in a closed well and the biochemical changes that are occurring in the water prior to reaching the monitor, as well as to the changes that are probably occurring prior to analyzing the grab samples in a field lab. Further investigation is required to determine the exact cause of this poor agreement.

The monitor served well in detecting and assessing the exceedences of the IJC

objectives. Even the relatively poor quality of the pH data did not hinder the achievement of this objective. The routine monthly samples were particularly deficient in describing the duration and severity of such exceedences and therefore can contribute little towards an assessment of biological impacts.

TDS and chloride exceeded the IJC objectives about 10% of the time, mostly during the winter. Since TDS is a greater concern during the winter periods, particularly in dry years, any additional input resulting either from the Garrison Diversion Unit project or discharges from Lake Ardoch during such periods would further exacerbate the problem.

Low DO during the summer is a natural phenomenon in the Red River. Therefore DO measurement is important during this period and precautions should be taken to avoid discharges that would further deplete the oxygen content during the summer periods. Mean DO concentration during the winter period was above 10 mg/L, yet generally, the Red River was undersaturated.

Conductivity and chloride exceedences always occurred during the winter periods and therefore measurements of these parameters during the winter periods are more important than during other periods of the year. It is noteworthy that, in contrast to the importance of monitoring for certain nutrients and biocides during the spring and fall, it is the summer and winter monitoring that is important for DO and major ions, respectively, in the Red River.

Although the conductivity and chloride concentrations were inversely related to the discharge, these relationships were not strong. Probable causes include discharges from Lake Ardoch, sugar mill molasses discharges and varying proportions of groundwater.

All parameters generally followed a seasonal pattern. As expected, it was most evident for temperature and DO. Despite such a succinct seasonal pattern, the chloride and to a lesser extent conductivity, varied substantially from year to year. These yearly variations were caused by the varying rate of river discharges

and outflow from Lake Ardoch. Prevention of sugar mill molasses discharges and the cessation of the saline water discharges from Lake Ardoch during the winter periods improved the water quality of the Red River.

Although statistically significant long-term increases in pH, conductivity and chloride and decreases in dissolved oxygen were detected, only the pH increase was conclusive.

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